Acta Cryst. (1994). B50, 772–779

Structure of Three Novel Photochromic Compounds; X-ray Crystallographic and Theoretical Studies

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(*Received* 19 *October* 1993; *accepted* 26 *May* 1994)

Abstract

(1) 5,7-Dimethoxy-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline], $C_{20}H_{22}N_2O_3$, $M_r = 338.4$, monoclinic, $P2_1/c$, $a = 12.151$ (2), $b = 12.090$ (4), $c = 24.836$ (4) Å, $\beta = 90.31$ (1)°, $V = 3648$ (2) Å^3, $Z = 8$, $D_x = 1.23$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.637$ mm^{-1}, $F(000) = 1440$, $T = 296$ K, $R = 0.063$ for 3106 unique observed reflections. (2) 5,5′,7-Trimethoxy-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline], $C_{21}H_{24}N_2O_4$, $M_r = 368.4$, monoclinic, $P2_1/c$, $a = 8.025$ (2), $b = 12.415$ (3), $c = 19.319$ (4) Å, $\beta = 99.31$ (2)°, $V = 1899.4$ (8) Å^3, $Z = 4$, $D_x = 1.288$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.084$ mm^{-1}, $F(000) = 784$, $T = 173$ K, $R = 0.0486$ for 1611 unique observed reflections. (3) 5′-Fluoro-5,7-dimethoxy-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline], $C_{20}H_{21}N_2O_3F$, $M_r = 356.4$, monoclinic, $P2_1/c$, $a = 11.484$ (3), $b = 13.832$ (2), $c = 11.511$ (1) Å, $\beta = 98.90$ (1)°, $V = 1810.4$ (6) Å^3, $Z = 4$, $D_x = 1.308$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.754$ mm^{-1}, $F(000) = 752$, $T = 173$ K, $R = 0.0468$ for 2229 unique observed reflections. These three monomeric compounds consist of a substituted benzoxazine ring orthogonally coupled to an indoline ring through a spiro C atom.

Introduction

Organic photochromic materials have broad commercial applications due to their ability to reversibly alter their spectroscopic characteristics. Additionally, these very important materials vary in color, intensity, rate of reaction, stability and solubility (Clegg, *et al.*, 1991, and references therein). In the past, development of these materials has occurred *via* synthesis of a large number of analogs followed by chemical purification, characterization and finally measurement of spectral properties. Recent advances have allowed for a more directed approach towards rational molecular design through the use of computational chemistry and X-ray diffractometry, coupled to organic synthesis methods. This paper examines a series of photochromic molecules and their properties through several spectroscopic techniques, as well as a semiempirical quantum mechanical method.

Crystallography

[Data for (2) and (3) are given in parentheses when they differ from those of (1)]. Colorless, parallelepiped shaped crystals, 0.14 × 0.23 × 0.31, (0.18 × 0.21 × 0.25) and (0.25 × 0.40 × 0.50 mm), were mounted along the largest dimension and data were collected with a Rigaku AFC-6*R* diffractometer equipped with a copper rotating anode and a highly oriented graphite monochromator. A constant scan speed of 8° min^{-1} in ω was used and the weak reflections, [$I < 5\sigma(I)$] for (1) and (2) and [$I < 6\sigma(I)$] for (3), were rescanned to a maximum of four times and the counts accumulated to assure good counting statistics. The intensities of three monitor reflections measured after every 200 reflections did not change significantly during 73, 28 and 34 h of X-ray exposure. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 25, 15 and 25 reflections $50 < 2\theta < 80$, ($40 < 2\theta < 60$) and ($60 <$

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$2\theta < 80°$): the data were corrected for Lorentz and polarization effects and not for absorption due to a low μ value. See Tables 1, 2 and 3 for cell parameters and other relevant data.

The systematic absences ($0k0$, $k = 2n+1$ and $h0l$, $l = 2n+1$) indicated the space group $P2_1/c$. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990*a*). For (1), the structure was refined by a block-diagonal least-squares matrix method as follows: O1*a* and O1*b* every cycle; O2*a*—C20*a* and O2*b*—C20*b* in alternate cycles with C25—C77. All non-H atoms were refined anisotropically and the function minimized was $\sum w(|F_o| - |F_c|)^2$. H atoms were placed in ideal positions with a fixed isotropic U value of 0.08 Å^2. For (2), all non-H atoms were refined anisotropically by the full-matrix least squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$. H atoms were placed in ideal positions with a fixed isotropic U value of 0.08 Å^2. For (3), all non-H atoms were refined anisotropically, while H atoms were refined isotropically by the full-matrix least squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$, with $g = 0.004$, 0.002 and 0.0015, was used. There was no evidence of secondary extinction; therefore, it was not applied. The refinement converged to the R indices given in Table 4, which also includes Δ/σ and $\Delta\rho_{max}$ in the last cycles of refinement. The final difference map was devoid of significant features.

All calculations were performed on a Silicon Graphics personal iris 4D/35 and an IBM compatible PC using the programs *TEXSAN* (Molecular Structure Corporation, 1985) for data reduction, *SHELXS*86 (Sheldrick, 1990*a*) for structure solution and *SHELXTL/PC* (Sheldrick, 1990*b*) for refinement and plotting. Final atomic coordinates are listed in Tables 5, 6 and 7, and selected bond lengths and angles are listed in Tables 8, 9 and 10.*

Table 1. *Summary of crystal data, data collection and structural refinement for* (1)

Crystal data	
Unit-cell parameters	
a (Å)	12.151 (2)
b (Å)	12.090 (4)
c (Å)	24.836 (4)
β (°)	90.31 (1)
Volume (Å^3)	3648 (2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14, C_{2h}^5)
Empirical formula	$C_{20}H_{22}N_2O_3$
Formula weight	338.4
z; $F(000)$	8; 1440
Density (calc.) (Mg m^{-3})	1.23
Absorption coefficient (μ) (mm^{-1})	0.637
Data collection	
Radiation	Cu $K\alpha$ (λ = 1.54178 Å)
Monochromator	Highly oriented graphite crystal
Temperature (K)	296
2θ range (°)	4.0–120.0
Scan type	2θ–θ
Scan speed (° min^{-1})	Constant; 8.00 in ω (for details see text)
Scan width	1.628 + 0.140tanθ
Scan time/background time	2:1
Index ranges	$0 \le h \le 13$, $0 \le k \le 13$, $-27 \le l \le 27$
Total reflections collected	6159
Independent reflections	5446 (R_{int} = 2.39%)
Unique data used (m)	3106 [$F > 4.0\sigma(F)$]
Solution and refinement	
No. of parameters refined (n)	451
Data-to-parameter ratio (m/n)	6.9:1
Final R indices (obs. data) (%)	R = 6.30, wR = 7.94
Goodness-of-fit (s)	2.43
Largest shift/error (Δ/σ)	0.018
Largest difference peak ($\Delta\rho_{max}$) (e Å^{-3})	0.58
Largest difference hole (e Å^{-3})	−0.30

$R = (\sum||F_o| - |F_c||/\sum|F_o|)$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $s = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.

Synthesis

Preparations of (1), (2) and (3) have been previously synthesized by Kwak & Hurditch (1989) and are crystallized and characterized as follows: The crude photochromic compounds were purified on a silica gel column using a mixture of ethyl acetate and hexane as the eluant. The photochromic fractions were collected and the solvent removed under vacuum. The products were crystallized using an ether–hexane mixture, and then collected by vacuum filtration. X-ray quality crystals were obtained by slow evaporation of a 50% mixture of ethyl acetate and hexane.

Spectroscopic data for (1) (*see Fig.* 1)

NMR, ^{1}H ($CDCl_3$): δ 1.29 (*s*, 3H, 3-Me), 1.34 (*s*, 3H, 3-Me), 2.76 (*s*, 3H, N-Me), 3.70 (*s*, 3H, H10′), 3.91 (*s*, 3H, H9′) 5.96 [*d*, 1H, H5′, J(H5′, H7′) = 2.4 Hz], 6.07 [*d*, 1H, H7′, J(H7′, H5′) = 2.4 Hz], 6.55 [*d*, 1H, H7, J(H7, H6) = 7.7 Hz], 6.86 [*d*, *d*, 1H, H5, J(H5, H4) = 7.4 Hz, J(H5, H6) = 7.4 Hz], 7.05 [*d*, *d*, 1H, H4, J(H4, H5) = 7.4 Hz, J(H4, H6) = 1.1 Hz], 7.18 [*d*, *d*, *d*, 1H, H6, J(H6, H7) = 7.7 Hz, J(H6, H5) = 7.4 Hz, J(H6, H4) = 1.1 Hz], 7.48 (*s*, 1H, H2′).

NMR, ^{13}C{^{1}H} ($CDCl_3$): δ 20.4 (Me), 25.3 (Me), 29.4 (N—Me), 51.6 (C3), 55.1 (10′), 55.8 (C9′), 91.7 (C5′), 92.0 (C7′), 98.7 (C 2/3′), 107.0 (C7), 114.5 (C1*a*′), 119.7 C(5), 121.3 (C4), 127.9 (C6), 135.8 (C4*a*), 147.6 (C7*a*), 148.0 (C2′), 148.9 (C4*a*′), 156.1 (C8′), 161.3 (C6′).

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates , torsion angles and least-squares planes data have been deposited with the IUCr (Reference: ST1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Summary of crystal data, data collection and structural refinement for* (2)

Crystal data	
Unit-cell parameters	
a (Å)	8.025 (2)
b (Å)	12.415 (3)
c (Å)	19.319 (4)
β (°)	99.31 (2)
Volume (Å^3)	1899.4 (8)
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14, C_{2h}^5)
Empirical formula	$C_{21}H_{24}N_2O_4$
Formula weight	368.4
z; $F(000)$	4; 784
Density (calc.) (Mg m^{-3})	1.288
Absorption coefficient (μ) (mm^{-1})	0.084
Data collection	
Radiation	Cu $K\alpha$ (λ = 1.54178 Å)
Monochromator	Highly oriented graphite crystal
Temperature (K)	173
2θ range (°)	4.0–118.0
Scan type	2θ–θ
Scan speed (° min^{-1})	Constant; 8.00 in ω (for details see text)
Scan width	1.418 + 0.140tanθ
Scan time/background time	2:1
Index ranges	$0 \le h \le 7$, $0 \le k \le 13$, $-21 \le l \le 21$
Total reflections collected	2401
Independent reflections	1995 (R_{int} = 0.50%)
Unique data used (m)	1611 [$F > 4.0\sigma(F)$]
Solution and refinement	
No. of parameters refined (n)	244
Data-to-parameter ratio (m/n)	6.6:1
Final R indices (obs. data) (%)	R = 4.86, wR = 7.49
Goodness-of-fit (s)	1.56
Largest shift/error (Δ/σ)	0.010
Largest difference peak ($\Delta\rho_{max}$) (e Å^{-3})	0.30
Largest difference hole (e Å^{-3})	−0.22

$R = (\sum||F_o| - |F_c||/\sum|F_o|)$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $s = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.

Table 3. *Summary of crystal data, data collection and structural refinement for* (3)

Crystal data	
Unit-cell parameters	
a (Å)	11.484 (3)
b (Å)	13.832 (2)
c (Å)	11.511 (1)
β (°)	98.90 (1)
Volume (Å^3)	1810.4 (6)
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14, C_{2h}^5)
Empirical formula	$C_{20}H_{21}N_2O_3F$
Formula weight	356.4
z; $F(000)$	4; 752
Density (calc.) (Mg m^{-3})	1.308
Absorption coefficient (μ) (mm^{-1})	0.754
Data collection	
Radiation	Cu $K\alpha$ (λ = 1.54178 Å)
Monochromator	Highly oriented graphite crystal
Temperature (K)	173
2θ range (°)	4.0–120.0
Scan type	2θ–θ
Scan speed (° min^{-1})	Constant; 8.00 in ω (for details see text)
Scan width	1.732 + 0.140tanθ
Scan time/background time	2:1
Index ranges	$-120 \le h \le 12$, $0 \le k \le 15$, $0 \le l \le 12$
Total reflections collected	3403
Independent reflections	2691 (R_{int} = 4.26%)
Unique data used (m)	2229 [$F > 6.0\sigma(F)$]
Solution and refinement	
No. of parameters refined (n)	319
Data-to-parameter ratio (m/n)	7.0:1
Final R indices (obs. data) (%)	R = 4.68, wR = 7.32
Goodness-of-fit (s)	1.74
Largest shift/error (Δ/σ)	0.001
Largest difference peak ($\Delta\rho_{max}$) (e Å^{-3})	0.33
Largest difference hole (e Å^{-3})	−0.26

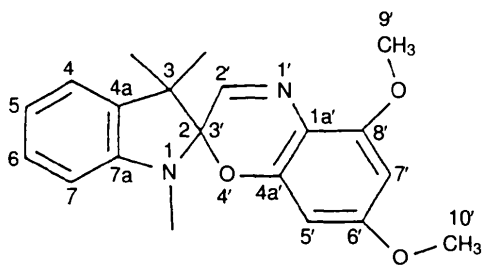
$R = (\sum||F_o| - |F_o||/\sum|F_o|)$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $s = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.

Mass spectra, m/z 471 (P); HRMS calc. for $C_{20}H_{22}O_3N_2 + Cs^+ = 471.0685$. Found: 471.0685; error: 0 m.m.u., 0 p.p.m.

Spectroscopic data for (2) (*see Fig.* 2)

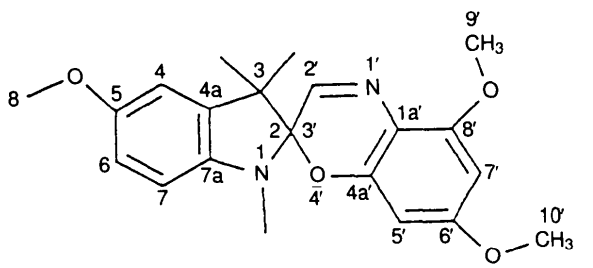
NMR, ^{1}H ($CDCl_3$): δ 1.27 (*s*, 3H, 3-Me), 1.31 (*s*, 3H, 3-Me), 2.75 (*s*, 3H, N—Me), 3.72 (*s*, 3H, H10′), 3.80 (*s*, 3H, H8), 3.92 (*s*, 3H, H9′), 5.98 [*d*, 1H, H5′, J(H5′, H7′) = 2.5 Hz], 6.07 [*d*, 1H, H7′, J(H7′, H5′) = 2.5 Hz], 6.15 [*d*, 1H, H4, J(H4, H6) = 2.2 Hz]; 6.37 [*d*, *d*, 1H, H6, J(H6, H4) = 2.2 Hz, J(H6, H7) = 8.0 Hz], 6.93 [*d*, 1H, H7, J(H7, H6) = 8.0 Hz], 7.46 (*s*, 1H, H2′).

NMR ^{13}C{^{1}H} ($CDCl_3$): δ 20.8 (Me), 25.6 (Me), 29.6 (N—Me), 51.3 (C3), 55.4 (C8 and C10′), 56.0



(1)

Fig. 1. 5,7-Dimethoxy-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline].



(2)

Fig. 2. 5.7-Dimethoxy-5′-methoxy-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline].

Table 4. *Compound* (1) *bond lengths* (Å)

	MM*	AM1†	EXP‡	EXP§
C1—C2	1.39	1.40	1.40	1.39
C2—C3	1.40	1.39	1.36	1.36
C3—C4	1.39	1.40	1.38	1.37
C5—C4	1.42	1.40	1.38	1.38
C5—C6	1.42	1.43	1.38	1.37
C6—C1	1.43	1.38	1.36	1.37
N1—C5	1.46	1.42	1.41	1.42
N1—C11	1.48	1.44	1.46	1.45
N1—C10	1.50	1.49	1.46	1.46
C6—C7	1.54	1.51	1.51	1.50
C7—C10	1.62	1.60	1.53	1.53
C7—C9	1.56	1.52	1.56	1.47
C7—C8	1.56	1.52	1.50	1.52
C10—O1	1.49	1.45	1.45	1.46
O1—C14	1.45	1.38	1.36	1.37
C14—C13	1.41	1.42	1.39	1.37
C13—N2	1.49	1.41	1.41	1.41
N2—C12	1.28	1.29	1.27	1.26
C12—C10	1.56	1.52	1.52	1.51
C14—C15	1.39	1.40	1.39	1.37
C15—C16	1.39	1.40	1.38	1.37
C16—O2	1.43	1.38	1.36	1.38
O2—C19	1.44	1.42	1.41	1.42
C16—C17	1.39	1.41	1.40	1.39
C17—C18	1.40	1.39	1.37	1.37
C18—O3	1.44	1.38	1.36	1.36
O3—C20	1.44	1.43	1.42	1.43
C18—C13	1.40	1.42	1.41	1.41

* Molecular mechanics with Biosym CVFF Force Field.
† AM1 semiempirical molecular orbital theory.
‡ Molecule *A* of (1) (crystal structure).
§ Molecule *B* of (1) (crystal structure).

(C9′), 92.0 (C5′), 92.0 C(7′), 95.1 (C4), 99.2 (C2/3′), 103.4 (C6), 114.6 (C1*a*′), 121.7 (C7), 128.5 (C4*a*), 148.3 (C2′), 149.0 (C4*a*′), 149.2 (C7*a*), 156.2 C(8′), 160.5 (C5), 161.4 (C6′).

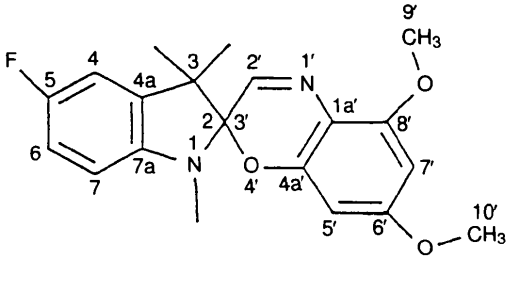
Mass spectra, *m/z* 501 (P), HRMS calc. for $C_{21}H_{24}O_4N_2 + Cs^+ = 501.0790$. Found: 501.0780; error: 1.0 m.m.u., 2.0 p.p.m.

Spectroscopic data for (3) (*see Fig.* 3)

NMR, ^1H ($CDCl_3$): δ 1.30 (*s*, 3H, 3-Me), 1.32 (*s*, 3H, 3-Me), 2.73 (*s*, 3H, N-Me); 3.73 (*s*, 3H, H10′), 3.92 (*s*, 3H, H9′), 5.97 [*d*, 1H, H5′, *J*(H5′, H7′) = 2.5 Hz], 6.08 [*d*, 1H, H7′, *J*(H7′, H5′) = 2.5 Hz], 6.44 [*d*, *d*, 1H, H7, *J*(H7, H6) = 8.4 Hz, *J*(H7, F) = 4.1 Hz], 6.78 [*d*, *d*, 1H, H4, *J*(H4, H6) = 2.6 Hz, *J*(H4, F) = 8.1 Hz], 6.86 [*d*, *d*, *d*, 1H, H6, *J*(H6, H7) = 8.4 Hz, *J*(H6, H4) = 2.6 Hz, *J*(H6, F) = 9.1 Hz]; 7.45 (*s*, 1H, H2′);

NMR, ^{13}C {^1H} ($CDCl_3$): δ 20.4 (Me), 25.2 (Me), 29.9 (N—Me), 51.8 [*d*, C3, *J*(C3, F) = 1.7 Hz], 55.5 (C10′), 56.1 (C9′), 91.9 (C5′), 92.1 (C7′), 99.2 (C2/3′), 107.3 [*d*, C7, *J*(C7, F) = 8.0 Hz], 109.5 [*d*, C4, *J*(C4, F) = 24.2 Hz], 113.6 [*d*, C6, *J*(C6, F) = 23.4 Hz], 114.5 (C1*a*′), 137.7 [*d*, C4*a*, *J*(C4*a*, F) = 7.1 Hz], 143.8 (C7*a*), 147.8 (C2′), 148.9 (C4*a*′), 156.2 (C8′), 157.7 [*d*, C5, *J*(C5, F) = 235.1 Hz], 161.4 (C6′).

Mass spectra, *m/z* 489 (P); HRMS calc. for $C_{20}H_{21}FO_3N_2 + Cs^+ = 489.0591$. Found: 489.0611; error: 2.0 m.m.u., 4.1 p.p.m.



(3)

Fig. 3. 5,7-Dimethoxy-5′-fluoro-1′,3′,3′-trimethylspiro[2*H*-1,4-benzoxazine-2,2′-indoline].

Table 5. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$) *for* (1)

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O(1*A*)	4845 (2)	2124 (2)	4759 (1)	47 (1)
O(2*A*)	8234 (3)	3291 (3)	5543 (1)	73 (1)
O(3*A*)	5232 (3)	2295 (3)	6651 (1)	66 (1)
N(1*A*)	3272 (3)	1265 (3)	4415 (2)	53 (1)
N(2*A*)	3950 (3)	1825 (3)	5789 (2)	51 (1)
C(1*A*)	3056 (4)	3665 (6)	3584 (3)	82 (3)
C(2*A*)	3055 (5)	3213 (9)	3065 (3)	110 (4)
C(3*A*)	3126 (5)	2105 (10)	2984 (3)	114 (4)
C(4*A*)	3203 (4)	1377 (6)	3411 (2)	86 (3)
C(5*A*)	3212 (3)	1834 (5)	3920 (2)	54 (2)
C(6*A*)	3139 (4)	2955 (4)	4006 (2)	55 (2)
C(7*A*)	3157 (4)	3168 (4)	4606 (2)	49 (2)
C(8*A*)	3790 (5)	4175 (4)	4774 (3)	80 (2)
C(9*A*)	1947 (5)	3281 (5)	4805 (3)	89 (3)
C(10*A*)	3654 (3)	2078 (3)	4805 (2)	45 (2)
C(11*A*)	3748 (5)	162 (4)	4435 (2)	77 (2)
C(12*A*)	3341 (4)	1739 (4)	5373 (2)	53 (2)
C(13*A*)	5019 (3)	2246 (3)	5717 (2)	42 (2)
C(14*A*)	5458 (3)	2373 (3)	5204 (2)	40 (1)
C(15*A*)	6537 (3)	2702 (4)	5121 (2)	48 (2)
C(16*A*)	7178 (4)	2923 (4)	5569 (2)	51 (2)
C(17*A*)	6767 (4)	2808 (4)	6093 (2)	50 (2)
C(18*A*)	5703 (4)	2454 (4)	6163 (2)	47 (2)
C(19*A*)	8705 (4)	3412 (6)	5028 (2)	87 (3)
C(20*A*)	5898 (5)	2437 (7)	7117 (2)	109 (3)
O(1*B*)	10695 (2)	542 (3)	2444 (1)	54 (1)
O(2*B*)	9542 (3)	−181 (4)	4237 (1)	97 (2)
O(3*B*)	6918 (3)	505 (3)	2856 (2)	75 (1)
N(1*B*)	11242 (3)	1041 (3)	1582 (2)	55 (1)
N(2*B*)	8503 (3)	814 (3)	2113 (2)	58 (2)
C(1*B*)	12704 (5)	−1536 (4)	1552 (2)	70 (2)
C(2*B*)	13776 (4)	−1222 (6)	1436 (2)	81 (3)
C(3*B*)	14038 (5)	−132 (6)	1384 (2)	84 (3)
C(4*B*)	13262 (4)	684 (5)	1429 (2)	64 (2)
C(5*B*)	12189 (4)	365 (4)	1532 (2)	47 (2)
C(6*B*)	11917 (4)	−727 (4)	1599 (2)	51 (2)
C(7*B*)	10705 (4)	−799 (4)	1708 (2)	51 (2)
C(8*B*)	10397 (5)	−1662 (5)	2128 (3)	105 (3)
C(9*B*)	10087 (5)	−1103 (7)	1219 (3)	120 (4)
C(10*B*)	10433 (3)	387 (4)	1876 (2)	47 (2)
C(11*B*)	11342 (5)	2219 (4)	1678 (2)	78 (2)
C(12*B*)	9268 (4)	754 (4)	1772 (2)	62 (2)
C(13*B*)	8784 (4)	515 (4)	2646 (2)	45 (2)
C(14*B*)	9858 (4)	391 (4)	2807 (2)	46 (2)
C(15*B*)	10166 (4)	183 (4)	3330 (2)	58 (2)
C(16*B*)	9350 (5)	73 (5)	3703 (2)	65 (2)
C(17*B*)	8247 (4)	161 (4)	3562 (2)	62 (2)
C(18*B*)	7966 (4)	382 (4)	3040 (2)	53 (2)
C(19*B*)	10649 (6)	−401 (8)	4390 (3)	143 (4)
C(20*B*)	6039 (4)	340 (6)	3227 (3)	102 (3)

Table 6. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$) *for* (2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	7008 (3)	151 (2)	4156 (2)	59 (1)
O(2)	1274 (3)	3360 (2)	3496 (1)	35 (1)
O(3)	−2018 (3)	6524 (2)	3136 (1)	43 (1)
O(4)	−2430 (3)	3897 (2)	1329 (1)	50 (1)
N(1)	3971 (3)	4157 (2)	3920 (1)	37 (1)
N(2)	262 (4)	5334 (2)	4003 (2)	43 (1)
C(1)	8294 (5)	−140 (3)	3767 (2)	64 (2)
C(2)	6395 (4)	1191 (3)	4071 (2)	41 (1)
C(3)	4995 (4)	1402 (3)	4403 (2)	43 (1)
C(4)	4288 (4)	2422 (3)	4331 (2)	34 (1)
C(5)	4957 (4)	3201 (3)	3940 (2)	33 (1)
C(6)	6320 (4)	2989 (3)	3627 (2)	40 (1)
C(7)	7055 (4)	1983 (3)	3697 (2)	42 (1)
C(8)	2817 (4)	2916 (3)	4627 (2)	40 (1)
C(9)	1394 (5)	2124 (4)	4653 (2)	69 (2)
C(10)	3479 (6)	3337 (4)	5363 (2)	64 (2)
C(11)	2357 (4)	3849 (3)	4104 (2)	35 (1)
C(12)	4025 (5)	4912 (3)	3350 (2)	46 (1)
C(13)	1468 (5)	4800 (3)	4359 (2)	45 (1)
C(14)	−346 (4)	4970 (3)	3318 (2)	33 (1)
C(15)	146 (4)	3991 (3)	3073 (2)	32 (1)
C(16)	−514 (4)	3576 (3)	2422 (2)	34 (1)
C(17)	−1710 (4)	4188 (3)	1993 (2)	36 (1)
C(18)	−2226 (4)	5190 (3)	2209 (2)	38 (1)
C(19)	−1567 (4)	5573 (3)	2868 (2)	37 (1)
C(20)	−3366 (4)	7114 (3)	2727 (2)	50 (1)
C(21)	−2007 (5)	2866 (3)	1088 (2)	53 (1)

Table 7. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$) *for* (3)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
F(1)	8628 (2)	4750 (2)	4220 (2)	76 (1)
O(1)	4837 (1)	1939 (1)	5517 (1)	37 (1)
O(2)	1916 (1)	843 (1)	7683 (1)	44 (1)
O(3)	929 (2)	1315 (1)	3568 (2)	51 (1)
N(1)	6767 (2)	1797 (1)	6496 (2)	39 (1)
N(2)	4156 (2)	1419 (1)	7690 (2)	37 (1)
C(1)	8210 (2)	3977 (2)	4781 (2)	49 (1)
C(2)	7254 (2)	4149 (2)	5362 (2)	41 (1)
C(3)	6822 (2)	3368 (2)	5903 (2)	31 (1)
C(4)	7340 (2)	2459 (2)	5871 (2)	36 (1)
C(5)	8307 (2)	2314 (2)	5294 (2)	47 (1)
C(6)	8731 (2)	3094 (2)	4739 (2)	52 (1)
C(7)	5829 (2)	3304 (1)	6617 (2)	31 (1)
C(8)	4720 (2)	3870 (2)	6100 (2)	42 (1)
C(9)	6265 (2)	3660 (2)	7873 (2)	44 (1)
C(10)	5617 (2)	2187 (2)	6598 (2)	32 (1)
C(11)	6893 (3)	766 (2)	6310 (3)	54 (1)
C(12)	5173 (2)	1776 (2)	7657 (2)	38 (1)
C(13)	3360 (2)	1409 (1)	6633 (2)	31 (1)
C(14)	3701 (2)	1678 (1)	5566 (2)	32 (1)
C(15)	2926 (2)	1667 (1)	4512 (2)	35 (1)
C(16)	1783 (2)	1358 (2)	4533 (2)	37 (1)
C(17)	1421 (2)	1057 (2)	5580 (2)	39 (1)
C(18)	2200 (2)	1090 (1)	6620 (2)	35 (1)
C(19)	741 (3)	534 (3)	7717 (3)	63 (1)
C(20)	1229 (3)	1631 (2)	2480 (3)	55 (1)

Theoretical methods

Theoretical studies were carried out *via* molecular mechanics (Biosym CVFF Force Field; Biosym Technologies, 1992) and semiempirical quantum mechanical (AM1; Dewar, Zoebich, Healy & Stewart, 1985) methods. Geometric parameters for

Table 8. *Bond lengths* (Å) *and angles* (°) *for* (1)

O(1*A*)—C(10*A*)	1.454 (5)	O(1*A*)—C(14*A*)	1.364 (5)
O(2*A*)—C(16*A*)	1.360 (6)	O(2*A*)—C(19*A*)	1.413 (6)
O(3*A*)—C(18*A*)	1.358 (5)	O(3*A*)—C(20*A*)	1.419 (6)
N(1*A*)—C(5*A*)	1.412 (6)	N(1*A*)—C(10*A*)	1.456 (6)
N(1*A*)—C(11*A*)	1.456 (6)	N(2*A*)—C(12*A*)	1.274 (6)
N(2*A*)—C(13*A*)	1.407 (5)	C(1*A*)—C(2*A*)	1.400 (11)
C(1*A*)—C(6*A*)	1.361 (9)	C(2*A*)—C(3*A*)	1.359 (16)
C(3*A*)—C(4*A*)	1.382 (11)	C(4*A*)—C(5*A*)	1.380 (8)
C(5*A*)—C(6*A*)	1.377 (8)	C(6*A*)—C(7*A*)	1.512 (7)
C(7*A*)—C(8*A*)	1.500 (7)	C(7*A*)—C(9*A*)	1.560 (7)
C(7*A*)—C(10*A*)	1.532 (6)	C(10*A*)—C(12*A*)	1.518 (6)
C(13*A*)—C(14*A*)	1.391 (6)	C(13*A*)—C(18*A*)	1.405 (6)
C(14*A*)—C(15*A*)	1.387 (6)	C(15*A*)—C(16*A*)	1.380 (6)
C(16*A*)—C(17*A*)	1.402 (7)	C(17*A*)—C(18*A*)	1.374 (6)
O(1*B*)—C(10*B*)	1.456 (5)	O(1*B*)—C(14*B*)	1.375 (5)
O(2*B*)—C(16*B*)	1.380 (6)	O(2*B*)—C(19*B*)	1.420 (9)
O(3*B*)—C(18*B*)	1.359 (6)	O(3*B*)—C(20*B*)	1.429 (7)
N(1*B*)—C(5*B*)	1.418 (6)	N(1*B*)—C(10*B*)	1.460 (6)
N(1*B*)—C(11*B*)	1.451 (7)	N(2*B*)—C(12*B*)	1.263 (6)
N(2*B*)—C(13*B*)	1.412 (6)	C(1*B*)—C(2*B*)	1.388 (8)
C(1*B*)—C(6*B*)	1.374 (7)	C(2*B*)—C(3*B*)	1.363 (10)
C(3*B*)—C(4*B*)	1.370 (8)	C(4*B*)—C(5*B*)	1.385 (7)
C(5*B*)—C(6*B*)	1.373 (7)	C(6*B*)—C(7*B*)	1.501 (7)
C(7*B*)—C(8*B*)	1.524 (8)	C(7*B*)—C(9*B*)	1.471 (8)
C(7*B*)—C(10*B*)	1.532 (7)	C(10*B*)—C(12*B*)	1.505 (6)
C(13*B*)—C(14*B*)	1.371 (6)	C(13*B*)—C(18*B*)	1.408 (7)
C(14*B*)—C(15*B*)	1.374 (6)	C(15*B*)—C(16*B*)	1.367 (7)
C(16*B*)—C(17*B*)	1.387 (8)	C(17*B*)—C(18*B*)	1.366 (7)

C(10*A*)—O(1*A*)—C(14*A*)	118.8 (3)	C(16*A*)—O(2*A*)—C(19*A*)	117.6 (4)
C(18*A*)—O(3*A*)—C(20*A*)	118.0 (4)	C(5*A*)—N(1*A*)—C(10*A*)	105.4 (4)
C(5*A*)—N(1*A*)—C(11*A*)	119.7 (4)	C(10*A*)—N(1*A*)—C(11*A*)	118.2 (4)
C(12*A*)—N(2*A*)—C(13*A*)	117.3 (4)	C(2*A*)—C(1*A*)—C(6*A*)	117.6 (7)
C(1*A*)—C(2*A*)—C(3*A*)	121.5 (8)	C(2*A*)—C(3*A*)—C(4*A*)	121.4 (7)
C(3*A*)—C(4*A*)—C(5*A*)	116.5 (7)	N(1*A*)—C(5*A*)—C(4*A*)	127.1 (5)
N(1*A*)—C(5*A*)—C(6*A*)	110.3 (4)	C(4*A*)—C(5*A*)—C(6*A*)	122.6 (5)
C(1*A*)—C(6*A*)—C(5*A*)	120.4 (5)	C(1*A*)—C(6*A*)—C(7*A*)	130.8 (5)
C(5*A*)—C(6*A*)—C(7*A*)	108.8 (4)	C(6*A*)—C(7*A*)—C(8*A*)	114.7 (4)
C(6*A*)—C(7*A*)—C(9*A*)	108.5 (4)	C(8*A*)—C(7*A*)—C(9*A*)	108.9 (4)
C(6*A*)—C(7*A*)—C(10*A*)	100.1 (4)	C(81)—C(7*A*)—C(10*A*)	114.2 (4)
C(9*A*)—C(7*A*)—C(10*A*)	110.1 (4)	O(1*A*)—C(10*A*)—N(1*A*)	106.7 (3)
O(1*A*)—C(10*A*)—C(7*A*)	109.4 (3)	N(1*A*)—C(10*A*)—C(7*A*)	104.1 (3)
O(1*A*)—C(10*A*)—C(12*A*)	109.8 (3)	N(1*A*)—C(10*A*)—C(12*A*)	110.8 (4)
C(7*A*)—C(10*A*)—C(12*A*)	115.6 (4)	N(2*A*)—C(12*A*)—C(10*A*)	125.8 (4)
N(2*A*)—C(13*A*)—C(14*A*)	121.1 (4)	N(2*A*)—C(13*A*)—C(18*A*)	120.4 (4)
C(14*A*)—C(13*A*)—C(18*A*)	118.3 (4)	O(1*A*)—C(14*A*)—C(13*A*)	120.5 (4)
O(1*A*)—C(14*A*)—C(15*A*)	117.1 (4)	C(13*A*)—C(14*A*)—C(15*A*)	122.3 (4)
C(14*A*)—C(15*A*)—C(16*A*)	117.8 (4)	O(2*A*)—C(16*A*)—C(15*A*)	123.6 (4)
O(2*A*)—C(16*A*)—C(17*A*)	114.6 (4)	C(15*A*)—C(16*A*)—C(17*A*)	121.7 (4)
C(16*A*)—C(17*A*)—C(18*A*)	119.2 (4)	O(3*A*)—C(18*A*)—C(13*A*)	115.4 (4)
O(3*A*)—C(18*A*)—C(17*A*)	124.0 (4)	C(13*A*)—C(18*A*)—C(17*A*)	120.6 (4)
C(10*B*)—O(1*B*)—C(14*B*)	177.4 (3)	C(16*B*)—O(2*B*)—C(19*B*)	117.0 (4)
C(18*B*)—O(3*B*)—C(20*B*)	118.0 (4)	C(5*B*)—N(1*B*)—C(10*B*)	106.2 (4)
C(5*B*)—N(1*B*)—C(11*B*)	121.0 (4)	C(10*B*)—N(1*B*)—C(11*B*)	120.5 (4)
C(12*B*)—N(2*B*)—C(13*B*)	116.0 (4)	C(2*B*)—C(1*B*)—C(6*B*)	118.4 (5)
C(1*B*)—C(2*B*)—C(3*B*)	120.3 (6)	C(2*B*)—C(3*B*)—C(4*B*)	121.9 (5)
C(3*B*)—C(4*B*)—C(5*B*)	117.6 (5)	N(1*B*)—C(5*B*)—C(4*B*)	128.4 (4)
N(1*B*)—C(5*B*)—C(6*B*)	110.5 (4)	C(4*B*)—C(5*B*)—C(6*B*)	121.2 (4)
C(1*B*)—C(6*B*)—C(5*B*)	120.6 (4)	C(1*B*)—C(6*B*)—C(7*B*)	131.1 (5)
C(5*B*)—C(6*B*)—C(7*B*)	108.3 (4)	C(6*B*)—C(7*B*)—C(8*B*)	114.1 (4)
C(6*B*)—C(7*B*)—C(9*B*)	111.3 (4)	C(8*B*)—C(7*B*)—C(9*B*)	105.5 (5)
C(6*B*)—C(7*B*)—C(10*B*)	102.0 (4)	C(8*B*)—C(7*B*)—C(10*B*)	113.6 (4)
C(9*B*)—C(7*B*)—C(10*B*)	110.4 (4)	O(1*B*)—C(10*B*)—N(1*B*)	105.7 (3)
O(1*B*)—C(10*B*)—C(7*B*)	109.8 (4)	N(1*B*)—C(10*B*)—C(7*B*)	103.0 (3)
C(1*B*)—C(10*B*)—C(12*B*)	109.2 (4)	N(1*B*)—C(10*B*)—C(12*B*)	112.9 (4)
C(7*B*)—C(10*B*)—C(12*B*)	115.7 (4)	N(2*B*)—C(12*B*)—C(10*B*)	126.6 (4)
N(2*B*)—C(13*B*)—C(14*B*)	121.8 (4)	N(2*B*)—C(13*B*)—C(18*B*)	120.9 (4)
C(14*B*)—C(13*B*)—C(18*B*)	117.2 (4)	O(1*B*)—C(14*B*)—C(13*B*)	119.9 (4)
O(1*B*)—C(14*B*)—C(15*B*)	116.5 (4)	O(13*B*)—C(14*B*)—C(15*B*)	123.4 (4)
C(14*B*)—C(15*B*)—C(16*B*)	117.6 (5)	O(2*B*)—C(16*B*)—C(15*B*)	123.6 (4)
O(2*B*)—C(16*B*)—C(17*B*)	114.7 (5)	C(15*B*)—C(16*B*)—C(17*B*)	121.6 (5)
C(16*B*)—C(17*B*)—C(18*B*)	119.4 (5)	O(3*B*)—C(18*B*)—C(13*B*)	114.6 (4)
O(3*B*)—C(18*B*)—C(17*B*)	124.7 (4)	C(13*B*)—C(18*B*)—C(17*B*)	120.6 (4)

Table 9. *Bond lengths* (Å) *and angles* (°) *for* (2)

O(1)—C(1)	1.418 (5)	O(1)—C(2)	1.382 (4)
O(2)—C(11)	1.474 (4)	O(2)—C(15)	1.364 (4)
O(3)—C(19)	1.361 (4)	O(3)—C(20)	1.434 (4)
O(4)—C(17)	1.368 (4)	O(4)—C(21)	1.422 (5)
N(1)—C(5)	1.423 (4)	N(1)—C(11)	1.448 (4)
N(1)—C(12)	1.453 (5)	N(2)—C(13)	1.278 (4)
N(2)—C(14)	1.409 (4)	C(2)—C(3)	1.405 (5)
C(2)—C(7)	1.375 (5)	C(3)—C(4)	1.385 (5)
C(4)—C(5)	1.388 (5)	C(4)—C(8)	1.521 (5)
C(5)—C(6)	1.359 (5)	C(6)—C(7)	1.379 (5)
C(8)—C(9)	1.515 (6)	C(8)—C(10)	1.528 (5)
C(8)—C(11)	1.542 (5)	C(11)—C(13)	1.508 (5)
C(14)—C(15)	1.384 (5)	C(14)—C(19)	1.414 (4)
C(15)—C(16)	1.384 (4)	C(16)—C(17)	1.388 (4)
C(17)—C(18)	1.396 (5)	C(18)—C(19)	1.381 (5)

C(1)—O(1)—C(2)	116.8 (3)	C(11)—O(2)—C(15)	119.2 (2)
C(19)—O(3)—C(20)	117.2 (3)	C(17)—O(4)—C(21)	117.3 (3)
C(5)—N(1)—C(11)	106.8 (3)	C(5)—N(1)—C(12)	118.3 (3)
C(11)—N(1)—C(12)	119.6 (3)	C(13)—N(2)—C(14)	117.1 (3)
O(1)—C(2)—C(3)	114.5 (3)	O(1)—C(2)—C(7)	124.8 (3)
C(3)—C(2)—C(7)	120.7 (3)	C(2)—C(3)—C(4)	118.0 (3)
C(3)—C(4)—C(5)	120.2 (3)	C(3)—C(4)—C(8)	131.4 (3)
C(5)—C(4)—C(8)	108.3 (3)	N(1)—C(5)—C(4)	109.5 (3)
N(1)—C(5)—C(6)	129.4 (3)	C(4)—C(5)—C(6)	121.1 (3)
C(5)—C(6)—C(7)	119.6 (3)	C(2)—C(7)—C(6)	120.3 (3)
C(4)—C(8)—C(9)	112.7 (3)	C(4)—C(8)—C(10)	108.3 (3)
C(9)—C(8)—C(10)	109.9 (3)	C(4)—C(8)—C(11)	100.1 (3)
C(9)—C(8)—C(11)	114.1 (3)	C(10)—C(8)—C(11)	111.3 (3)
O(2)—C(11)—N(1)	110.4 (3)	O(2)—C(11)—C(8)	105.1 (3)
N(1)—C(11)—C(8)	103.3 (2)	O(2)—C(11)—C(13)	109.6 (2)
N(1)—C(11)—C(13)	111.3 (3)	C(8)—C(11)—C(13)	116.8 (3)
N(2)—C(13)—C(11)	126.1 (3)	N(2)—C(14)—C(15)	121.9 (3)
N(2)—C(14)—C(19)	120.5 (3)	C(15)—C(14)—C(19)	117.6 (3)
O(2)—C(15)—C(14)	119.9 (3)	O(2)—C(15)—C(16)	116.7 (3)
C(14)—C(15)—C(16)	123.3 (3)	C(15)—C(16)—C(17)	117.7 (3)
O(4)—C(17)—C(16)	124.2 (3)	O(4)—C(17)—C(18)	114.5 (3)
C(16)—C(17)—C(18)	121.3 (3)	C(17)—C(18)—C(19)	119.6 (3)
O(3)—C(19)—C(14)	115.2 (3)	O(3)—C(19)—C(18)	124.3 (3)
C(14)—C(19)—C(18)	120.5 (3)		

Table 10. *Bond lengths* (Å) *and angles* (°) *for* (3)

F(1)—C(1)	1.374 (3)	O(1)—C(10)	1.457 (2)
O(1)—C(14)	1.363 (3)	O(2)—C(18)	1.358 (3)
O(2)—C(19)	1.422 (4)	O(3)—C(16)	1.364 (3)
O(3)—C(20)	1.419 (4)	N(1)—C(4)	1.391 (3)
N(1)—C(10)	1.448 (3)	N(1)—C(11)	1.452 (3)
N(2)—C(12)	1.274 (3)	N(2)—C(13)	1.404 (3)
C(1)—C(2)	1.391 (4)	C(1)—C(6)	1.365 (4)
C(2)—C(3)	1.377 (3)	C(3)—C(4)	1.393 (3)
C(3)—C(7)	1.508 (3)	C(4)—C(5)	1.394 (3)
C(5)—C(6)	1.380 (4)	C(7)—C(8)	1.535 (3)
C(7)—C(9)	1.536 (3)	C(7)—C(10)	1.564 (3)
C(10)—C(12)	1.503 (3)	C(13)—C(14)	1.397 (3)
C(13)—C(18)	1.402 (3)	C(14)—C(15)	1.389 (3)
C(15)—C(16)	1.385 (3)	C(16)—C(17)	1.396 (3)
C(17)—C(18)	1.379 (3)		

C(10)—O(1)—C(14)	119.5 (2)	C(18)—O(2)—C(19)	117.5 (2)
C(16)—O(3)—C(20)	117.6 (2)	C(4)—N(1)—C(10)	107.9 (2)
C(4)—N(1)—C(11)	120.3 (2)	C(10)—N(1)—C(11)	119.3 (2)
C(12)—N(2)—C(13)	117.0 (2)	F(1)—C(1)—C(2)	116.9 (2)
F(1)—C(1)—C(6)	119.5 (2)	C(2)—C(1)—C(6)	123.6 (3)
C(1)—C(2)—C(3)	116.7 (2)	C(2)—C(3)—C(4)	120.7 (2)
C(2)—C(3)—C(7)	130.4 (2)	C(4)—C(3)—C(7)	108.9 (2)
N(1)—C(4)—C(3)	110.0 (2)	N(1)—C(4)—C(5)	128.8 (2)
C(3)—C(4)—C(5)	121.2 (2)	C(4)—C(5)—C(6)	118.2 (2)
C(1)—C(6)—C(5)	119.7 (2)	C(3)—C(7)—C(8)	114.3 (2)
C(3)—C(7)—C(9)	109.3 (2)	C(8)—C(7)—C(9)	109.4 (2)
C(3)—C(7)—C(10)	100.4 (2)	C(8)—C(7)—C(10)	112.4 (2)
C(9)—C(7)—C(10)	110.9 (2)	O(1)—C(10)—N(1)	106.9 (2)
O(1)—C(10)—C(7)	108.6 (2)	N(1)—C(10)—C(7)	103.1 (2)
O(1)—C(10)—C(12)	111.2 (2)	N(1)—C(10)—C(12)	110.7 (2)
C(7)—C(10)—C(12)	115.7 (2)	N(2)—C(12)—C(10)	126.8 (2)

Table 10 (*cont.*)

N(2)—C(13)—C(14)	121.8 (2)	N(2)—C(13)—C(18)	120.2 (2)
C(14)—C(13)—C(18)	118.0 (2)	O(1)—C(14)—C(13)	120.5 (2)
O(1)—C(14)—C(15)	117.1 (2)	C(13)—C(14)—C(15)	122.4 (2)
C(14)—C(15)—C(16)	118.0 (2)	O(3)—C(16)—C(15)	124.3 (2)
O(3)—C(26)—C(17)	114.6 (2)	C(15)—C(16)—C(17)	121.1 (2)
C(16)—C(17)—C(18)	120.0 (2)	O(2)—C(18)—C(13)	115.4 (2)
O(2)—C(18)—C(17)	124.1 (2)	C(13)—C(18)—C(17)	120.5 (2)

Table 11. *Compound* (1) *bond angles* (°)

	MM*	AM1†	EXP‡	EXP§
C1—C2—C3	121.1	120.4	121.5	120.3
C2—C3—C4	121.1	121.5	121.4	121.9
C3—C4—C5	119.3	118.4	116.5	117.6
C4—C5—C6	119.6	120.0	122.6	121.2
C5—C6—Cl	119.9	120.8	120.4	120.6
C6—Cl—C2	119.0	119.0	117.6	118.4
C4—C5—N1	128.8	127.9	127.1	128.4
C5—N1—C11	121.4	118.0	119.7	121.0
C5—N1—C10	107.6	107.5	105.4	106.2
C1—C6—C7	129.2	128.9	130.8	131.1
C6—C7—C9	107.7	110.7	108.5	111.3
C6—C7—C8	111.7	111.2	114.7	114.1
C6—C7—C10	101.2	102.2	100.1	102.0
C7—C10—O1	110.5	105.6	109.4	109.8
C7—C10—C12	114.5	112.8	115.6	115.7
N1—C10—O1	101.1	109.9	106.7	105.7
N1—C10—C12	110.4	109.0	110.8	112.9
C10—C12—N2	121.6	126.5	125.8	126.6
C12—N2—C13	123.3	177.7	117.3	116.0
N2—C13—C14	118.8	120.4	121.1	121.8
C13—C14—O1	119.4	122.4	120.5	119.9
C14—O1—C10	120.8	118.6	118.8	117.4
C14—C15—C16	120.2	118.1	117.8	117.6
C15—C16—O2	120.1	124.0	123.6	123.6
C15—C16—C17	119.9	121.4	121.7	121.6
C16—O2—C19	115.8	116.3	117.6	117.0
C16—C17—C18	120.6	119.6	119.2	119.4
C17—C18—O3	118.2	116.5	124.0	124.7
C17—C18—C13	119.5	121.0	120.6	120.6
C18—O3—C20	115.9	114.8	118.0	118.0
C18—C13—C14	119.6	117.5	118.3	117.2
C13—C14—C15	120.2	122.4	122.3	123.4
O1—C14—C15	120.5	115.1	117.1	116.5
O1—C14—C13	119.4	122.4	120.5	119.9
N2—C13—C14	118.8	120.4	121.1	121.8
N2—C13—C18	121.6	122.1	120.8	120.9

* Molecular mechanics with Biosym CVFF Force Field.
† AM1 semiempirical molecular orbital theory.
‡ Molecule *A* of (1) (crystal structure).
§ Molecule *B* of (1) (crystal structure).

theoretical and experimental results were within coincidence by 0.02–0.04 Å for bond lengths and 2–3° bond angles, with minor exceptions. The calculated bond lengths and angles are summarized and compared with the crystallographic results in Tables 4 and 11 for (1), Tables 12 and 13 for (2), and in Tables 14 and 15 for (3), respectively.

As can been seen in Tables 4, 12 and 14, the agreement between the theoretical and crystallographic bond lengths is within 0.002–0.004 Å, with few exceptions. As can be seen in Tables 11, 13 and 15, theoretical bond angles agree to within 2–3° of the experimental values, with few exceptions. In Tables 4 and 12–15, the AM1 data are generally similar to the crystallographic data and in better agreement than the molecular mechanics CVFF

Table 12. *Compound* (2) *bond lengths* (Å)

	MM*	AM1†	EXP‡
O1—C1	1.44	1.42	1.42
O1—C2	1.43	1.39	1.38
C2—C7	1.40	1.40	1.38
C2—C3	1.39	1.41	1.40
C3—C4	1.43	1.38	1.38
C7—C6	1.39	1.40	1.38
C6—C5	1.42	1.40	1.36
C5—C4	1.42	1.43	1.39
C4—C8	1.54	1.51	1.52
C8—C10	1.56	1.52	1.53
C8—C11	1.62	1.60	1.54
C11—N1	1.50	1.49	1.45
N1—C12	1.48	1.44	1.45
N1—C5	1.46	1.42	1.42
C11—O2	1.49	1.45	1.47
O2—C15	1.45	1.38	1.36
C15—C14	1.41	1.42	1.38
C14—N2	1.49	1.41	1.41
N2—C13	1.28	1.29	1.28
C13—C11	1.56	1.52	1.50
C15—C16	1.39	1.40	1.38
C16—C17	1.39	1.40	1.39
C17—C18	1.39	1.41	1.40
C18—C19	1.40	1.39	1.38
C19—C14	1.40	1.42	1.41
C19—O3	1.44	1.38	1.36
O3—C20	1.44	1.43	1.43
C17—O4	1.43	1.38	1.37
O4—C21	1.44	1.42	1.42

* Molecular mechanics with Biosym CVFF Force Field (Biosym Technologies, 1992).
† AM1 semiempirical molecular orbital theory.
‡ Crystal structure.

Table 13. *Compound* (2) *bond angles* (°)

	MM*	AM1†	EXP‡
C1—O1—C2	115.9	114.7	116.8
O1—C2—C7	119.6	122.7	124.8
O1—C2—C3	119.6	115.6	114.5
C2—C3—C4	119.2	118.0	118.0
C3—C4—C5	119.9	120.9	120.2
C4—C5—C6	119.7	120.5	121.1
C5—C6—C7	119.3	118.7	119.6
C6—C7—C2	121.2	120.4	120.3
C3—C4—C8	129.2	128.7	131.4
C4—C8—C9	111.7	111.2	112.7
C4—C8—C10	107.6	110.6	108.3
C4—C8—C11	101.2	102.1	100.1
C4—C5—N1	111.6	112.0	109.5
C5—N1—C11	107.6	107.4	106.8
C5—N1—C12	121.4	117.6	118.3
C12—N1—C11	130.8	117.0	119.6
N1—C11—C8	107.1	107.0	103.3
N1—C11—O2	101.1	110.0	110.4
N1—C11—C13	110.5	108.9	111.3
C9—C8—C11	114.3	111.9	114.1
C10—C8—C11	116.7	111.4	111.3
C8—C11—C13	114.5	112.6	116.8
C8—C11—O2	110.5	105.5	105.1
C11—O2—C15	120.8	118.6	119.2
C11—C13—N2	121.6	126.5	126.1
C13—N2—C14	123.3	117.8	117.1
N2—C14—C15	118.8	120.4	121.9
C14—C15—O2	119.4	122.4	119.9
N2—C14—C19	121.6	122.1	121.9
C14—C19—C18	119.5	121.0	120.5
C14—C19—O3	122.2	122.1	115.2
C19—O3—C20	115.9	114.8	117.2
O3—C19—C18	118.2	116.7	124.3
C19—C18—C17	120.6	119.5	119.6
C18—C17—O4	120.0	114.6	114.5
C17—O4—C21	115.8	116.3	117.3
O4—C17—C16	120.1	124.0	124.2
C17—C16—C15	120.2	118.1	117.7
C16—C15—C14	120.2	122.4	123.3
C16—C15—O2	120.4	115.1	116.7
O2—C15—C14	119.4	122.4	119.9

* Molecular mechanics with Biosym CVFF Force Field (Biosym Technologies, 1992).
† AM1 semiempirical molecular orbital theory.
‡ Crystal structure.

force-field study results (Biosym Technologies, 1992). However, the molecular mechanics results are likely to improve, as more accurate force fields are developed.

The differences in bond lengths or angles which are >0.002 Å or 2–3° are likely due to phase and temperature differences. The experimental studies are in the crystal phase at either 173 or 296 K, while the theoretical studies are for isolated molecules at 0 K. In this respect, theoretical studies can be used to identify regions of molecules significantly impacted by phase changes or temperature differences.

With regard to relative changes in bond lengths and angles, as shown in Tables 4 and 11–15, both theoretical methods predict relative changes, in accord with the experiment. The few exceptions may be due to omission of crystal packing forces in the theoretical methods and temperature differences, as discussed above. Of particular interest is the C—O bond which is cleaved in each of the compounds when exposed to light. In comparing the bond lengths [C10—O1 for (1) and (3) and C11—O2 for

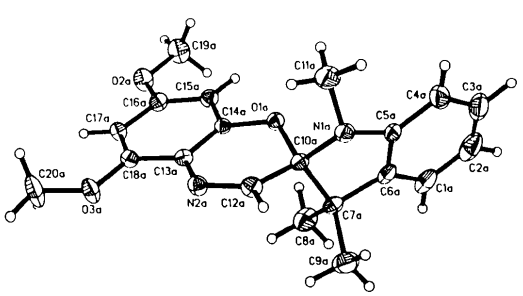


Fig. 4. Crystal structure of molecule *A* of (1). The non-H atoms are drawn with 30% probability ellipsoids, H atoms are drawn arbitrarily small. Molecule *B* is only slightly different in bond lengths and angles.

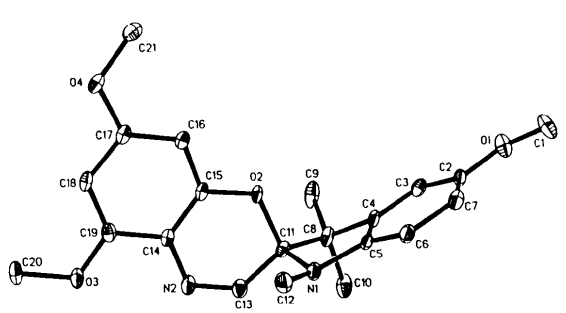


Fig. 5. Crystal structure of (2). The atoms are drawn with 30% probability ellipsoids.

Table 14. *Compound* (3) *bond lengths* (Å)

	MM*	AM1†	EXP‡	AXP§
C1—C2	1.39	1.41	1.39	1.40
C2—C3	1.43	1.38	1.38	1.38
C3—C4	1.42	1.43	1.39	1.38
C5—C4	1.42	1.40	1.39	1.38
C5—C6	1.39	1.40	1.38	1.36
C6—C1	1.40	1.40	1.36	1.36
F1—C1	1.36	1.36	1.37	1.39
N1—C4	1.46	1.42	1.39	1.40
N1—C11	1.48	1.44	1.45	1.44
N1—C10	1.50	1.49	1.45	1.45
C7—C10	1.62	1.60	1.56	1.55
C7—C9	1.56	1.52	1.54	1.53
C7—C8	1.56	1.52	1.53	1.52
C7—C3	1.54	1.51	1.51	1.51
C10—O1	1.49	1.45	1.46	1.45
O1—C14	1.45	1.38	1.36	1.36
C14—C13	1.41	1.42	1.40	1.39
C13—N2	1.49	1.41	1.40	1.40
N2—C12	1.28	1.29	1.27	1.27
C12—C10	1.56	1.52	1.50	1.51
C14—C15	1.39	1.40	1.39	1.39
C15—C16	1.39	1.40	1.39	1.37
C16—O3	1.43	1.38	1.36	1.36
O3—C20	1.44	1.42	1.42	1.42
C16—C17	1.39	1.41	1.40	1.39
C17—C18	1.40	1.39	1.38	1.38
C18—O2	1.44	1.38	1.36	1.36
O2—C19	1.44	1.43	1.42	1.42
C18—C13	1.40	1.42	1.40	1.40

* Molecular mechanics with Biosym CVFF Force Field (Biosym Technologies, 1992).
† AM1 semiempirical molecular orbital theory.
‡ Crystal structure at 173 K.
§ Crystal structure at 296 K.

(2)], as noted in Figs. 4, 5 and 6 for (1), (2) and (3), both theoretical methods predict no change in bond lengths, while experimental data show a maximum change of only 0.01 Å. Little or no change in the theoretical and experimental bond lengths indicates that it is unlikely there is significant differences in bond strengths in either isolated molecules or the crystal phase.

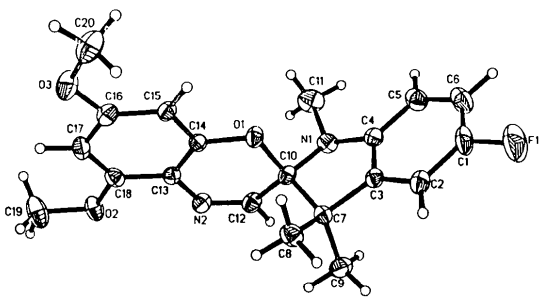


Fig. 6. Crystal structure of (3). The non-H atoms are drawn with 30% probability ellipsoids, while H atoms are drawn arbitrarily small.

Table 15. *Compound* (3) *bond angles* (°)

	MM*	AM1†	EXP‡	EXP§
C1—C2—C3	119.1	118.4	116.7	115.0
C2—C3—C4	119.9	121.1	120.7	121.2
C3—C4—C5	119.6	120.1	121.2	121.7
C4—C5—C6	119.2	119.0	118.2	118.3
C5—C6—C1	121.7	120.6	119.7	119.2
C6—C1—C2	121.0	120.9	123.6	124.5
F1—C1—C2	119.5	119.3	116.9	115.5
F1—C1—C6	119.5	119.8	119.5	119.9
C5—C4—N1	128.8	127.7	128.8	128.2
C2—C3—C7	129.2	128.6	130.4	129.9
C4—N1—C11	121.5	118.0	120.3	120.9
C4—N1—C10	107.6	107.5	107.9	107.4
N1—C10—C7	107.1	107.0	103.1	103.6
N1—C10—O1	101.1	109.9	106.9	107.0
N1—C10—C12	110.5	108.9	110.7	110.5
C10—C7—C8	114.3	112.0	112.4	112.6
C10—C7—C9	116.7	111.3	110.9	110.9
C10—C7—C3	101.2	102.1	100.4	100.5
C3—C7—C8	111.7	111.1	114.3	114.1
C3—C7—C9	107.7	110.7	109.3	109.0
C11—N1—C10	130.7	117.3	119.3	120.3
C10—C12—N2	121.6	126.4	126.8	127.2
C10—O1—C14	120.8	118.6	119.5	120.1
O1—C14—C13	119.4	122.4	120.5	120.5
O1—C14—C15	120.4	115.1	117.1	116.6
C14—C13—N2	118.8	120.4	121.8	121.9
C13—N2—C12	123.3	117.8	117.0	116.8
C12—C10—O1	112.3	112.7	111.2	110.9
C14—C15—C16	120.2	118.1	118.0	117.2
C15—C16—C17	119.9	121.4	121.1	121.9
C16—C17—C18	120.6	119.6	120.9	119.6
C17—C18—C13	119.5	121.0	120.5	120.5
C18—C13—C14	119.6	117.5	118.0	117.7
C13—C14—C15	120.2	122.5	122.4	123.0
C15—C16—O3	120.1	124.0	124.3	124.5
C16—O3—C20	115.8	116.4	117.6	117.9
O3—C16—C17	120.0	114.6	114.6	113.6
C17—C18—O2	118.2	116.5	124.1	124.1
C18—O2—C19	115.9	114.9	117.5	117.7
O2—C18—C13	122.2	122.3	115.4	115.4

* Molecular mechanics with CVFF Force Field (Biosym Technologies, 1992).
† AM1 semiempirical molecular orbital theory.
‡ Crystal structure at 173 K.
§ Crystal structure at 296 K.

References

Biosym Technologies (1992). Biosym CVFF Force Field. Software Program, Discover. BioSym Technologies, San Diego, CA, USA.

CLEGG, W., NORMAN, N. C., FLOOD, T., SALLANS, L., KWAK, W. S., KWIATKOWSKI, P. L. & LASCH, J. G. (1991). *Acta Cryst.* C**47**, 817–824.

DEWAR, M. J. S., ZOEBICH, E. G., HEALY, E. F. & STEWART, J. J. (1985). *J. Am. Chem. Soc.* **107**, 3902.

KWAK, W. S. & HURDITCH, R. J. (1989). United States Patent No. 4,816,584.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

SHELDRICK, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.

SHELDRICK, G. M. (1990*b*). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.