On the other hand, the method with symmetry-adapted functions always requires more parameters. Its use is mainly interesting when the molecular orientations are not really localized, because the librational anharmonicity is then taken into account. However, two problems may occur in this method which is available only for rigid molecules:

(i) When the translational amplitude is very important, as for HMDS, the Bragg reflections are only observable for small values, even if the molecular orientations are localized. It is then very difficult to deduce from the refinements the orientational molecular probability.

(ii) When the functions adapted to the molecular symmetry have negligible values for the atoms of the external shells of the molecule, the corresponding $A^l_{mm'}$ terms are only related to the internal shells and are not then easily refinable. In this case, occurring in HME, the molecular orientational probability deduced from the refinements is less localized than in reality, mainly at low temperature.

However, the comparative use of these two different methods gives a very accurate view of the long-range order in plastic crystals.

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Structural and Molecular-Orbital Study of the Furoxan Ring.* Structures of 3-Phenylfuroxan and 4-Phenylfuroxan and Comparison with Related Structures

BY M. CALLERI†

Dipartimento di Scienze della Terra, Università di Torino, Via San Massimo 22, 10123 Torino, Italy

G. RANGHINO

Istituto G. Donegani, Via Fauser 4, 28100 Novara, Italy

AND P. UGLIENGO AND D. VITERBO

Istituto di Chimica Fisica dell' Università, Corso M. D'Azeglio 48, 10125 Torino, Italy

Abstract

Ab initio and CNDO/2 molecular-orbital calculations have been performed for the positional isomer pairs of phenylfuroxan, methylfuroxancarboxamide, isopropyl *N*-(methylfuroxanyl)carbamate, and chloro(phenyl)furoxan, for the molecules of dimethylfuroxan, diphenylfuroxan, and furazan and for an idealized unsubstituted furoxan molecule. The furoxan ring appears to be electron-overcrowded, in

particular in furoxan itself, which has not been synthesized so far. This excess of charge is released toward the substituents in the derivatives. In all derivatives the furoxan group remains the most reactive part of the molecule. 3-Phenylfuroxan, (1A): $C_8H_6N_2O_2$, m.p. 380 K, $M_r = 162.1$, triclinic, $P\bar{1}$, $a = 6.438$ (1), $b = 7.017$ (2), $c = 9.151$ (1) Å, $\alpha = 74.75$ (1), $\beta = 72.05$ (1), $\gamma = 82.50$ (1)°, $U = 378.9$ (1) Å^3, $Z = 2$, $D_x = 1.42$ Mg m^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.9$ mm^{-1}, $F(000) = 168$, room temperature, $R = 0.051$ for 1254 independent diffractometer reflexions. 4-Phenylfuroxan, (1B): $C_8H_6N_2O_2$, m.p. 393 K, tri-

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* Furoxan is furazan *N*-oxide.
† To whom correspondence should be addressed.

clinic, $P\bar{1}$, $a = 5\cdot778$ (3), $b = 7\cdot674$ (5), $c = 9\cdot501$ (5) Å, $\alpha = 109\cdot99$ (4), $\beta = 102\cdot92$ (4), $\gamma = 95\cdot64$ (5)°, $U = 378\cdot7$ (4) Å^3, $Z = 2$, $D_x = 1\cdot42$ Mg m^{-3}, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot11$ mm^{-1}, $F(000) = 168$, room temperature, $R = 0\cdot051$ for 1231 independent diffractometer reflexions.

Introduction

In recent years several structural investigations on disubstituted furoxan derivatives have been carried out (e.g. Viterbo, Chiari & Calvino, 1982, and references therein). The geometrical features of the furoxan ring have been examined in detail with the aim of correlating them with the chemical properties of these derivatives (Gasco & Boulton, 1981, pp. 258–262). No systematic correlation could be made between the X-ray geometry of the ring and the nature of the substituents. This implies an important role for the electronic features of the furoxan ring both in the ground and in the higher-energy states.

Therefore, here we have added to the structural analysis of the two isomers of phenylfuroxan, (1A) and (1B), an ab initio and a semi-empirical CNDO/2 molecular-orbital study of the title and some other isomers: methylfuroxancarboxamide, (2A) and (2B); isopropyl N-(methylfuroxanyl)carbamate, (3A) and (3B) (Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1977, respectively); chloro(phenyl)furoxan, (4A), (4B1), (4B2) [there are two independent molecules in the asymmetric unit of (4B)] (Viterbo, Chiari & Calvino, 1982); and diphenylfuroxan, (6) (Sillitoe & Harding, 1978).

Calculations have also been performed for the furoxan molecule itself, which has not been synthesized so far, by reconstructing its geometry from that of (1B) on substituting the phenyl group by an H atom.

The same approach has been used for dimethylfuroxan, (5), by reconstructing its geometry from that of (3A) on substituting the isopropyl carbamate group by a methyl group; the relative positions of the two methyl groups have been chosen so as to minimize the total energy of the molecule.

Following the convention of regarding the N atom of the N-oxide function as the 2-position, Calvino, Gasco, Fruttero, Mortarini & Aime (1982) assigned the lower-melting isomer of the title pair as 3-phenylfuroxan, (1A), and the higher-melting isomer as 4-phenylfuroxan, (1B), on the basis of spectroscopic studies (^{13}C NMR spectroscopy). The X-ray analysis confirmed the assignment.

Experimental

Data collection

Crystals synthesized by Calvino et al. (1982) from ethanol–water as transparent, colourless, squat prisms. D_m not determined. Nicolet $R3$ four-circle diffractometer; intensity measurement at variable speed. Cell parameters from 15 reflexions ($15° \le 2\theta \le 30°$) for (1A) and from 25 reflexions ($30° \le 2\theta \le 40°$) for (1B).

(1A): crystal $0\cdot1 \times 0\cdot2 \times 0\cdot4$ mm; θ–2θ scan; scan speed from 4 to 29° min^{-1}; variable scan range as a function of $\alpha_1 - \alpha_2$ dispersion ($1\cdot9$–$2\cdot8°$); backgrounds measured in stationary mode, $0\cdot7$ times the peak scan time; one standard reflexion showed a constant intensity decay with a final drop of ~14%; 1386 reflexions measured ($h - 7, 5; k - 8, 8; l - 11, 0; 2\theta \le 140°$) and 1265 [with $I \ge 2\sigma(I)$] were considered as observed; 11 reflexions, exceeding 60 000 counts s^{-1} at pre-scan, were measured with the insertion of a Cu attenuator; however, these had to be discarded in the course of the refinement because of too poor F_o vs F_c agreement; intensities were corrected for decay, background and Lorentz–polarization effects, and placed on an absolute scale, by statistical methods, using the Nicolet (1980) suite of programs.

(1B): crystal $0\cdot2 \times 0\cdot2 \times 0\cdot7$ mm sealed in a Lindemann-glass capillary to prevent volatilization; ω scan; scan speed from 2 to 10° min^{-1}; scan range 1°; backgrounds measured in stationary mode, $0\cdot8$ times the peak scan time; one standard reflexion showed no decay; 1959 independent reflexions measured ($h - 8, 6; k - 10, 10; l$ 0, 13; $2\theta \le 60°$) and 1233 considered as observed and treated as for (1A); 9 reflexions were measured with the attenuator and two of these were discarded in the course of the refinement; because of the larger crystal dimensions, an empirical absorption correction was applied, based on the ψ-scan method (North, Phillips & Mathews, 1968) using 5 reflexions distributed over the 2θ range 11–36°.

Structure solution and refinement

(1A). Attempts to solve the structure in space group $P\bar{1}$ failed. Assuming symmetry $P1$, the MULTAN routine of the Nicolet (1980) system generated 32 sets of phases, using 191 reflexions with $|E| > 1\cdot50$. The E map from the most consistent set showed two quasi-centrosymmetric nine-atom fragments. After referring the coordinates to the centroid as origin, subsequent computation of a weighted difference Fourier map allowed the location of all non-hydrogen atoms which were refined (on F) by least-squares methods, using the SHELXTL system (Sheldrick, 1981). All H atoms were found on difference Fourier maps and isotropically refined with the constraints: C–H = $1\cdot01 \pm 0\cdot02$ and $2\cdot09 \pm 0\cdot04$ Å for the distances from H to the two adjacent C atoms in the phenyl ring or $2\cdot05 \pm 0\cdot04$ and $2\cdot20 \pm 0\cdot04$ Å for the distances of H(2) from N(2) and C(1) respectively (Fig. 1). A single isotropic thermal parameter common to all H atoms was refined and converged to $0\cdot087$ (3) Å^2. The

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$) *of compound* (1A), *with e.s.d.'s in parentheses*

	x	y	z	U^*_{eq}
C(1)	−1260 (2)	2277 (2)	1716 (2)	45 (1)
C(2)	−290 (2)	1763 (2)	2972 (2)	57 (1)
C(3)	−266 (2)	2570 (2)	18 (2)	44 (1)
C(4)	−1500 (3)	3144 (2)	−1055 (2)	55 (1)
C(5)	−475 (3)	3368 (3)	−2657 (2)	70 (1)
C(6)	1748 (3)	3049 (3)	−3218 (2)	70 (1)
C(7)	2991 (3)	2502 (3)	−2166 (2)	68 (1)
C(8)	1994 (2)	2266 (2)	−561 (2)	55 (1)
N(1)	−3383 (2)	2415 (2)	2407 (2)	56 (1)
N(2)	−1713 (2)	1600 (2)	4344 (2)	70 (1)
O(1)	−3722 (2)	1993 (2)	4084 (1)	71 (1)
O(2)	−5041 (2)	2801 (2)	1951 (2)	85 (1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$) *of compound* (1B), *with e.s.d.'s in parentheses*

	x	y	z	U^*_{eq}
C(1)	3160 (3)	868 (2)	3286 (2)	53 (1)
C(2)	4176 (4)	188 (3)	2052 (2)	70 (1)
C(3)	4358 (3)	2239 (2)	4869 (2)	53 (1)
C(4)	6679 (3)	3220 (3)	5226 (2)	64 (1)
C(5)	7785 (4)	4527 (3)	6711 (2)	76 (1)
C(6)	6592 (4)	4853 (3)	7840 (2)	78 (1)
C(7)	4281 (4)	3874 (3)	7495 (2)	81 (1)
C(8)	3160 (4)	2561 (3)	6015 (2)	67 (1)
N(1)	874 (3)	100 (3)	2859 (2)	78 (1)
N(2)	2505 (3)	−1025 (2)	859 (2)	74 (1)
O(1)	340 (3)	−1130 (2)	1334 (1)	85 (1)
O(2)	2392 (3)	−2060 (2)	−481 (2)	106 (1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

weighting scheme used in the closing cycles is $w = 1/[\sigma^2(F_o) + GF_o^2]$, where σ is the standard deviation of F_o and G a variable parameter. At convergence (mean $\Delta/\sigma < 0.04$) $R = 0.051$, $wR = 0.061$ ($G = 0.00138$), goodness of fit $= 1.968$ for 128 parameters and 1254 reflexions. No correction for secondary extinction. Residual fluctuations in the final difference Fourier synthesis were ± 0.20 eÅ^{-3}. Table 1 gives the coordinates and equivalent isotropic thermal parameters of (1A).

(1B). The solution was not straightforward for this isomer either. *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), with 298 $|E| > 1.30$, 3 reflexions in the starting set, generated 16 sets of phases. From the best E map were obtained the coordinates of all non-hydrogen atoms of a molecule which, however, was displaced from the correct position. The coordinates referred to an arbitrary origin were used for the Karle (1968) recycling procedure assuming $P1$ symmetry. Two molecules, related by an inversion centre, were obtained and partially refined before returning to the true $P\bar{1}$ symmetry. The least-squares refinement (on F) then proceeded successfully following the same procedure as for (1A). The isotropic thermal parameter common to all H atoms converged to

Table 3. *Bond distances* (Å) *and angles* (°) *of compound* (1A), *with e.s.d.'s in parentheses*

C(1)–C(2)	1·417 (2)	C(1)–C(3)	1·456 (2)
C(1)–N(1)	1·320 (2)	C(2)–N(2)	1·293 (2)
C(3)–C(4)	1·395 (2)	C(3)–C(8)	1·395 (2)
C(4)–C(5)	1·385 (2)	C(5)–C(6)	1·373 (3)
C(6)–C(7)	1·384 (3)	C(7)–C(8)	1·384 (2)
N(1)–O(1)	1·436 (2)	N(1)–O(2)	1·235 (2)
N(2)–O(1)	1·366 (2)		
C(2)–C(1)–C(3)	130·4 (1)	C(2)–C(1)–N(1)	104·9 (1)
C(3)–C(1)–N(1)	124·6 (1)	C(1)–C(2)–N(2)	112·8 (1)
C(1)–C(3)–C(4)	122·2 (1)	C(1)–C(3)–C(8)	119·1 (1)
C(4)–C(3)–C(8)	118·7 (1)	C(3)–C(4)–C(5)	119·8 (1)
C(4)–C(5)–C(6)	121·2 (2)	C(5)–C(6)–C(7)	119·5 (2)
C(6)–C(7)–C(8)	120·1 (1)	C(3)–C(8)–C(7)	120·7 (2)
C(1)–N(1)–O(1)	108·2 (1)	C(1)–N(1)–O(2)	135·4 (1)
O(1)–N(1)–O(2)	116·4 (1)	C(2)–N(2)–O(1)	106·6 (1)
N(1)–O(1)–N(2)	107·4 (1)		

0.094 (3) Å^2. At convergence (mean $\Delta/\sigma < 0.01$) $R = 0.051$, $wR = 0.052$ ($G = 0.00041$), goodness of fit $= 1.705$, for 128 parameters and 1231 reflexions. No correction for secondary extinction. Residual fluctuations in the final difference map were ± 0.15 e Å^{-3}. Table 2 gives the coordinates and equivalent isotropic thermal parameters of (1B).* Bond distances and angles for (1A) and (1B) are given in Tables 3 and 4, respectively. The numbering scheme is that already adopted for several other isomer pairs.

Ab initio and CNDO/2 calculations

HF–SCF *ab initio* (*IBMOL* program, Pavani & Gianolio, 1977) using a minimal Gaussian basis set (Corongiu & Clementi, 1978), and semi-empirical CNDO/2 calculations (Pople & Beveridge, 1970) have been performed for the six derivatives (1A), (1B), (2A), (2B), (3A) and (3B) and for the idealized

(1) R = −C₆H₅, R′ = H
(3) R = −CH₃, R′ = −NHCOOCH(CH₃)₂
(5) R = R′ = CH₃
(7) R = R′ = H

(2) R = −CH₃, R′ = −CONH₂
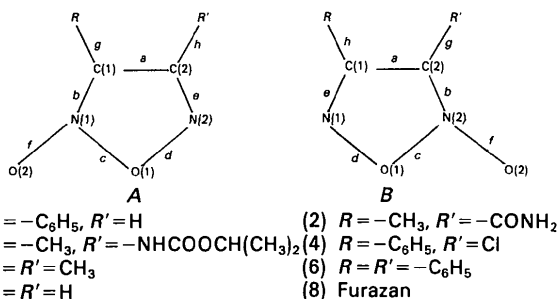(4) R = −C₆H₅, R′ = Cl
(6) R = R′ = −C₆H₅
(8) Furazan

Fig. 1. The furoxan isomers considered, with the labels for the atoms and bonds used throughout the text. Isomer (4B) has been treated in the two slightly different conformations, (4B1) and (4B2), present as independent molecules in the X-ray structure.

Table 4. *Bond distances (Å) and angles (°) of compound (1B), with e.s.d.'s in parentheses*

C(1)–C(2)	1·394 (3)	C(1)–C(3)	1·469 (2)
C(1)–N(1)	1·304 (2)	C(2)–N(2)	1·302 (2)
C(3)–C(4)	1·380 (2)	C(3)–C(8)	1·383 (3)
C(4)–C(5)	1·381 (2)	C(5)–C(6)	1·368 (3)
C(6)–C(7)	1·376 (3)	C(7)–C(8)	1·381 (2)
N(1)–O(1)	1·376 (2)	N(2)–O(1)	1·426 (2)
N(2)–O(2)	1·232 (2)		
C(2)–C(1)–C(3)	127·9 (2)	C(2)–C(1)–N(1)	110·2(1)
C(3)–C(1)–N(1)	121·9 (2)	C(1)–C(2)–N(2)	108·4 (2)
C(1)–C(3)–C (4)	120·4 (2)	C(1)–C(3)–C(8)	120·1 (1)
C(4)–C(3)–C(8)	119·4 (1)	C(3)–C(4)–C(5)	120·2 (2)
C(4)–C(5)–C(6)	120·3 (2)	C(5)–C(6)–C(7)	119·8 (2)
C(6)–C(7)–C(8)	120·4 (2)	C(3)–C(8)–C(7)	119·8 (2)
C(1)–N(1)–O(1)	107·3 (2)	C(2)–N(2)–O(1)	107·0 (2)
C(2)–N(2)–O(2)	136·3 (2)	O(1)–N(2)–O(2)	116·7 (1)
N(1)–O(1)–N(2)	107·2 (1)		

Table 5. *Total and binding energies* (a.u.): *ab initio and CNDO/2 (in parentheses) values*

$$1 \text{ a.u.} \equiv 4 \cdot 3594 \times 10^{-18} \text{ J.}$$

	Total energy	Binding energy
(1A)	−562·771909 (−121·470)	∼1·03655 (−10·000)
(1B)	−562·744998 (−121·445)	−1·00964 (−9·9754)
(2A)	−540·176472 (−122·439)	−0·49850 (−7·1096)
(2B)	−540·181207 (−122·464)	−0·50320 (−7·1332)
(3A)	−653·584712 (−149·524)	−0·67076 (−8·6694)
(3B)	−653·572938 (−149·502)	−0·65890 (−8·6477)
(4A)	(−136·945)	(−10·067)
(4B1)	(−136·952)	(−10·074)
(4B2)	(−136·959)	(−10·081)
(5)	(−93·1840)	(−6·3743)
(6)	(−166·869)	(−15·854)
(7)	−334·124282 (−75·8820)	−0·08202 (−3·9568)
(8)	(−57·4430)	(−3·6000)

furoxan (7). In the latter case the net charges and the overlap populations were computed according to Mulliken (1955).

CNDO/2 calculations have also been performed for other disubstituted furoxan derivatives, (4A), (4B), (5), (6), and on furazan (Saegebarth & Cox, 1965).

The non-hydrogen-atom coordinates from the X-ray analyses have been introduced, but the H atoms were placed in standard calculated positions.

The total and binding energies are listed in Table 5; the net charges on several pertinent atoms are given in Table 6; Table 7 illustrates the HOMO and LUMO energies. Dipole moments and overlap populations computed in the CNDO/2 approximation are reported in Table 8.

The deorthogonalized procedure proposed by McIver, Coppens & Nowak (1971) has been used, following Pisani, Ricca & Roetti (1971/1972), to obtain the eigenvector and density matrices.

Results and discussion

Figs. 2(a) and 2(b) show *ORTEP*II (Johnson, 1976) projections of the molecules of (1A) and (1B) onto the mean planes through the five-membered rings.

Table 6. *Ab initio and CNDO/2 net charges*

The last column is the sum of the net charges on the six atoms of the furoxan moiety. All the numbers are in (a.u.)×100. The primed values in columns (4) and (6) refer to the primed atom in the heading.

	C(1)	C(2)	N(1) or N(2)'	O(1)	N(2) or N(1)'	O(2)	R	R'	Sum
(a) Ab initio									
(1A)	7	−16	−1'	−14	20'	−26	−2	27	−30
(1B)	9	−18	−4	−14	21	−26	−1	27	−32
(2A)	10	5	−4'	−14	20'	−27	−76	42	−10
(2B)	12	3	−4	−14	20	−28	−76	49	−11
(3A)	7	22	−5'	−14	19'	−28	−76	−50	1
(3B)	10	18	−4	−15	19	−27	−76	−49	1
(7)	−13	−19	−3	−14	21	−26	27	28	−54
(b) CNDO/2									
(1A)	3	18	−6'	−14	23'	−31	6	27	−17
(1B)	17	−7	−10	−14	26	−31	1	11	−19
(2A)	17	8	−7'	−14	23'	−32	−13	46	−15
(2B)	21	−6	−10	−13	25	−30	−17	50	−11
(3A)	1	31	−11'	−13	24'	−31	−13	−40	1
(3B)	16	17	−9	−14	22	−31	−17	−37	1
(4A)	3	19	−5'	−13	24'	−30	7	−11	−2
(4B1)	17	5	−9	−13	25	−28	2	−8	−3
(4B2)	18	4	−10	−13	27	−27	2	−9	−1
(5)	17	3	−10	−14	23	−31	−18	−14	−12
(6)	−1	15	−11	−15	27	−31	6	1	−16
(7)	11	−5	−7	−13	26	−31	7	12	−20
(8)	7	7	−5	−13	−5		4	4	−8

Table 7. *Ab initio and CNDO/2 (in parentheses) energies* (a.u.) *for the HOMO and LUMO orbitals*

Type	HOMO	LUMO
(1A)	−0·3841 (−0·3804)	−0·0058 (0·0485)
(1B)	−0·4000 (−0·4056)	0·0014 (0·0520)
(2A)	−0·3923 (−0·3956)	0·0104 (0·0406)
(2B)	−0·4074 (−0·4151)	0·0009 (0·0423)
(3A)	−0·3884 (−0·4016)	0·0278 (0·0585)
(3B)	−0·3819 (−0·3878)	0·0275 (0·0584)
(4A)	(−0·3950)	(0·0353)
4B1)	(−0·4109)	(0·0359)
4B2)	(−0·4084)	(0·0373)
(5)	(−0·3902)	(0·0606)
(6)	(−0·3728)	(0·0631)
(7)	−0·4050 (−0·4138)	0·0169 (0·0536)
(8)	(−0·5146)	(0·0984)

The furazan ring is planar in both molecules and only slightly rotated with respect to the phenyl ring [3·5 (1) and 8·8 (1)° in (1A) and (1B), respectively].

The geometry of the furoxan moiety follows the pattern typical of this ring in disubstituted derivatives (Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1976, 1977) in the solid state.

The total energy differences for all three pairs of isomers (Table 5) show that isomer A is more stable when R' is H or isopropyl carbamate, whilst the opposite obtains with the carboxamide derivative in agreement with former studies on the isomerization equilibrium (Gasco & Boulton, 1973; Gasco, Mortarini, Ruà & Menziani, 1972; Calvino *et al.*, 1982).

Table 8. *Overlap populations* ($\times 10^2$) *of the bonds indicated in Fig.* 1 *and total dipole moments, both computed in the CNDO/2 approximation*

| | Bonds | | | | | | | | Dipole moment (Debye)* | |
	a	b	c	d	e	f	g	h	Calculated	Experimental
(1A)	981	901	463	440	931	491	885	802	4·47	
(1B)	990	943	464	431	878	490	818	866	5·12	
(2A)	954	915	461	446	882	475	888	832	3·79	
(2B)	938	875	462	420	889	516	850	876	1·24	
(3A)	961	929	459	424	882	482	887	791	7·07	
(3B)	971	949	461	429	887	467	780	881	6·82	
(4A)	960	895	452	438	902	500	860	458	3·26	
(4B1)	947	917	447	427	874	501	467	863	4·44	
(4B2)	951	891	453	418	875	524	471	867	4·22	
(5)	963	911	458	432	886	488	889	881	5·18	5·26†
(6)	968	882	466	427	872	525	858	875	4·89	4·81†
(7)	1016	948	464	437	905	488	818	790	4·28	
(8)	942	932	459	459	932		781	781	3·52	3·38‡

* 1 Debye $\equiv 3\cdot34 \times 10^{-30}$ C m.
† Borello & Lanfranco (1959).
‡ Saegebarth & Cox (1965).

From Table 6 it appears that the net charges on the atoms of the furoxan moiety are almost unaffected by the nature of the substituents and by the geometry of the moiety itself. This is particularly apparent for the N–O–N → O group whilst C(1) and C(2) are somewhat sensitive to the nature of the substituent. The last column of Table 6 reports the sum of the net atomic charges of the six atoms of the furoxan moiety. For the unsubstituted furoxan molecule this value is −0·54 a.u. which reduces to −0·30 in (1A) and (1B) and to −0·10 and 0·04 in derivatives (2) and (3), respectively.

The CNDO/2 values show a similar trend and we can infer that the furoxan ring is electron-density rich and tends to release its negative charge towards the substituents. The non-existence of the unsubstituted furoxan and the lability of monosubstituted furoxans (Gasco & Boulton, 1981, p. 321) could be related to the reduced possibility of delocalizing this excess of charge.

The features of the HOMO's and LUMO's give information on the reactivity of the molecules, and in Table 7 we report the energy values. In the case of the idealized furoxan the HOMO, with π sym-

metry, is mainly localized on C(2), N(1), N(2) and O(2), with relative weights of 0·5, 0·5, 0·2, 0·7. It may be added that, according to our results, the last-but-one occupied orbital is also localized on the above atoms with some contribution from O(1): its population analysis, however, indicates that this orbital is prevailingly the lone pair of O(2) since 80% of the electron density is on this atom. The lone pairs of N(1) and O(1) are directed inwards much more. The LUMO is delocalized over the whole molecule and also has π symmetry. The HOMO's of all the other compounds present the same features as for furoxan with some additional contributions: in (1A) from the C adjacent to the ring and from the *ortho* and *para* C atoms of the phenyl; in (2B) from the O of the amide group; in (4A) from the same atoms as in (1A) while in (4B1) and (4B2) from Cl; in (6) from the *ortho* and *para* C atoms of the phenyl attached to C(1).

The features of the (1A) HOMO are in agreement with Calvino, Ferrarotti, Gasco, Serafino & Pelizetti (1983), who found a preferential *ortho, para* substitution during the nitration reaction. Also, the contributions of the atomic orbitals to the LUMO's are nearly the same as for furoxan. The electronic structure of the furoxan group seems to be little influenced by the nature of the substituents or by geometrical differences. In all derivatives the ring is the most reactive moiety. The delocalization of the LUMO over all the atoms of the furoxan group is in agreement with the variety of reactions shown by these derivatives (Gasco & Boulton, 1981).

The analysis of the trend of bond energies (Fischer & Kollmar, 1970; and Clementi, 1976, and references therein) (Fig. 3) shows practically constant values for each bond in disubstituted furoxans, confirming the slight sensitivity of this nucleus to the nature of the substituents. Appreciable changes may be noted only in furoxan, and in (1A) and (1B) but these changes are more pronounced for the sequence of
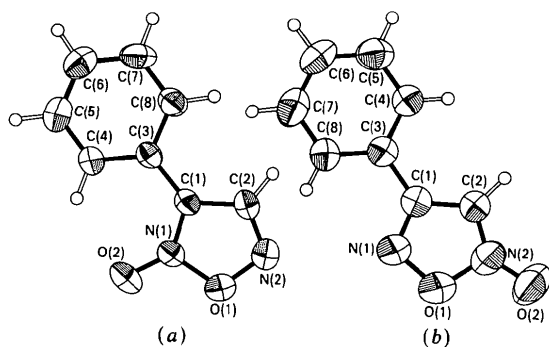

Fig. 2. ORTEPII (Johnson, 1976) projections of (*a*) isomer (1A) and (*b*) isomer (1B) on the plane through their five-membered rings. Thermal ellipsoids are drawn at the 50% probability level.

Table 9. *Differences in total energy, overlap populations for selected bonds (cf. Fig. 1) and total dipole moments for molecule (2B) at different rotation angles (θ) of the amide group around bond g*

$\theta(°)$	ΔE^* (kJ mol^{-1})	Overlap populations ($\times 10^2$)				Dipole moment (Debye)
		f	b	g	C=O	
0	0·0	515	875	850	768	1·24
20	7·04	513	879	848	769	1·92
45	22·5	504	891	840	773	3·40
60	31·0	498	901	834	776	4·30
80	38·8	494	909	828	778	5·38
90	40·6	494	911	828	779	5·84
100	40·9	496	910	830	779	6·22
120	37·5	504	903	837	777	6·78
180	20·7	526	880	858	770	7·25

* $\Delta E = E[(2B); \theta] - E[(2B); 0]$.

bonds b,a,e than for bonds c,d,f. In isomers $(1A)$ and $(1B)$ the comparison of the pairs of bonds b,e and c,d shows that the bonds closer to the H atom are weakened while the corresponding bonds closer to the phenyl ring are strengthened by an almost equal amount. This is in agreement with our previous remark about the stabilizing effect of the substituents capable of decreasing the electron density of the furoxan group.

In order to analyse in more detail the electronic effects caused by the substituents on the ring we have considered the isomers of (2). For $(2B)$ a certain degree of delocalization would be consistent with the planarity of the molecule found in the crystal (Calleri *et al.*, 1975); this and the possibility of a weak interaction between O(2) and one of the H atoms of the NH$_2$ was given as an explanation of the higher stability of this isomer with respect to $(2A)$ (Calleri *et al.*, 1975; Gasco & Boulton, 1973). Indeed, in the crystal
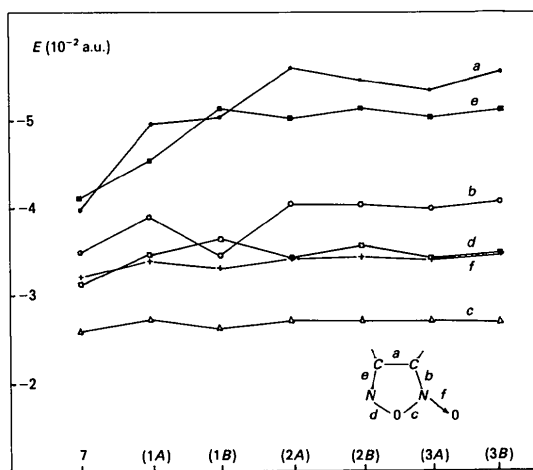
of the latter, the amide group is rotated with respect to the furoxan ring and the delocalization cannot take place. In order to verify this hypothesis we have computed, in the CNDO/2 approximation, the variation of the total energy and of the overlap populations in $(2B)$ when the amide group is rotated around bond g as a rigid fragment. As shown in Table 9, the rotation increases the total energy by up to 42 kJ mol^{-1}. The overlap population analysis is in agreement with the possibility of delocalization in the planar form actually found in the solid state.

The same analysis for isomer $(2A)$ shows only small changes both in energy and in overlap population and, therefore, the packing forces play a dominant role in determining the solid-state conformation.

Fig. 3. Bond energies (a.u.) for the bonds of the furoxan ring (*cf.* Fig. 1). All values are from the *ab initio* calculation.

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Charge Density Distribution of a Polymethine Cyanine Dye: (5-Dimethylamino-2,4-pentadienylidene)dimethylammonium Perchlorate

BY MASAKO HONDA, CHUJI KATAYAMA AND JIRO TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku 464, Japan

Abstract

$C_9H_{17}N_2^+ . ClO_4^-$ (orange form), $M_r = 252 \cdot 71$, monoclinic, $P2_1/a$, $a = 13 \cdot 671(3)$, $b = 14 \cdot 899(2)$, $c = 6 \cdot 186(2)$ Å, $\beta = 97 \cdot 27(2)°$, $V = 1249 \cdot 9(5)$ Å^3, $Z = 4$, $D_x = 1 \cdot 343$ g cm^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71073$ Å, $\mu = 2 \cdot 606$ cm^{-1}, $F(000) = 536$, $T = 140$ K, $R = 0 \cdot 045$ for 4331 independent data. A slight alternation is found in the bond lengths of the conjugated system of the polymethine cyanine dye [C–C distances $1 \cdot 376(2)$, $1 \cdot 399(2)$, $1 \cdot 378(2)$ and $1 \cdot 394(2)$ Å at 140 K]. The charge distribution is estimated by the method of Coppens, Guru Row, Leung, Stevens, Becker & Yang [*Acta Cryst.* (1979), A35, 63–72] and the result is in good agreement with the *ab initio* MO calculation. In particular, positive charges are found at the methyl groups [except C(11)] and the odd-numbered C atoms in the chain; negative charges are observed at C(4), C(11) and the N atoms.

Introduction

The crystal structure of the title compound (5DMP) is of particular interest because it provides a prototype of the cyanine dye structure. It has several modifications. The structure of the orange form of the perchlorate and that of the chloride were studied by Kulpe and co-workers (Sieber, Kutschabsky & Kulpe, 1974; Ziemer & Kulpe, 1975). The structure of the yellow form of the perchlorate was studied by Selzer & Matthews (1976) and Chentli-Benchikha, Declercq, Germain, Van Meerssche & Michel (1977). The orange form has crystal symmetry $P2_1/a$; accordingly, the accurate structure may be found because the crystal symmetry is not coincident with the molecular symmetry. An alternation of the bond length in the conjugated double bonds is important in the structural chemistry of polymethine cyanine dyes, and a precise X-ray structural study was under-

taken on one of the crystal modifications of 5DMP. Recently, Sano & Tanaka (1985) studied the reflection spectra of single crystals of 5DMP, and the orange crystal is found to show an intermolecular charge-transfer band while the yellow form exhibits quasi-metallic reflectivity which is rather unusual for a simple organic dye (Anex & Simpson, 1960). It is important to find the correlation between the crystal structure and spectra for polymorphic crystals.

Coppens and co-workers (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) have proposed a method for estimating the charge distribution in a molecule by an accurate X-ray structure analysis. The cyanine dye has a positive charge in the molecule; therefore, their method may be useful to find the charge distribution in the cation dye. Estimation of the charge distribution in the cation molecule may be a challenge to both the X-ray method and the theoretical study by *ab initio* MO calculation. In this study both methods show excellent agreement, but a few deviations from the predicted charge densities are found which may be ascribed to specific interionic interactions such as hydrogen bonding.

Experimental

The crystals of the orange form grown from a methanol solution were provided by Mr N. Sano. The size of the crystals was less than 0·5 mm and they were polished into a spherical form. The X-ray reflection data were collected by an AFC-5R Rigaku automated four-circle diffractometer at 140 and 296 K. For intensity measurement at 140 K all reflections were measured within a sphere of $2\theta \le 65°$ and half the sphere was recorded for $65° \le 2\theta \le 75°$. A total of 22 525 reflections were measured and averaged to give 6798 independent data. Other experimental conditions are in Table 1. The crystallographic data at 296 and 140 K are shown in Table 2, where we have