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Investigation of the Geometry of Substituted Dinitroanilines. II. Structural Study of *N*-Cyclohexyl-*N*-isopropyl-2,4-dinitroaniline in the Solid State and in Solution*

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Abstract. $C_{15}H_{21}N_3O_4$, monoclinic, $P2_1/n$, $M_r = 307{\cdot}3$, $a = 11{\cdot}601\,(6)$, $b = 11{\cdot}223\,(4)$, $c = 12{\cdot}143\,(4)$ Å, $\beta = 97{\cdot}75\,(2)°$, $V = 1567\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}30$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}89$ cm^{-1}, $F(000) = 656$, room temperature, final $R = 0{\cdot}043$, $wR = 0{\cdot}051$ for 1948 observed independent reflections. The molecule in the solid state is significantly non-planar, the dialkyl-substituted amino and *o*-nitro groups being rotated out of the benzene ring. The isopropyl moiety is *anti* to the *ortho* substituent in order to minimize intramolecular interactions. The cyclohexane ring, perpendicular to the amino group, adopts a chair conformation. Deformations observed in the aromatic ring skeleton could not be accounted for by the additivity of the substituent effects. ^{13}C NMR data allow us to infer that the molecule in solution has the amino and *o*-nitro groups twisted out of the mean ring plane, in agreement with single-crystal results.

Introduction. It has been found that several crystalline substituted nitroanilines exhibit useful quadratic nonlinear optical properties (Barzoukas, Josse, Fremaux, Zyss, Nicoud & Morley, 1987; Panunto, Urbánczyk-Lipowska, Johnson & Etter, 1987). Therefore, we have undertaken the present study as part of an investigation of the effects of bulky substituents on optical properties, geometry and packing of *N*,*N*-dialkyl-substituted dinitroanilines (Nudelman, Socolovsky & De Waisbaum, 1982; Punte, Rivero, Socolovsky & Nudelman, 1987, 1989).

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Experimental. The title compound was synthesized according to a procedure similar to that described by Brady & Cropper (1950) and crystallized by slow evaporation from methanol. A yellowish, irregular-shaped crystal of approximate dimensions 0·2 × 0·25 × 0·3 mm was used for data collection. The measurements were performed on an automatic four-circle Huber diffractometer with graphite-monochromated Mo *Kα* radiation. Lattice parameters were obtained from the setting angles of 20 reflections in the range $18{\cdot}5 < 2\theta < 34°$. Systematic absences indicated the space group to be $P2_1/n$, unique axis *b*. Data were collected in the ω step scan mode, scan width 1°, scan speed 0·77–4·62° $\min^{-1}$, to $2\theta_{\max} = 50°$, index range *h*: 0,13; *k*: 0,13; *l*: −14,14. Three standard reflections (111, $1\bar{1}1$, 208) measured every 90 min showed 2% intensity variation. Lorentz and polarization corrections were applied. Isotropic secondary-extinction correction of the form $F' = F(1 - CF^2/\sin\theta)$ was applied on F_c, refined *C* value: $8{\cdot}07 \times 10^{-3}$. No absorption correction was applied. From 3777 intensities measured (2740 unique, $R_{\text{int}} = 0{\cdot}019$), 1948 were considered observed using the criterion $I > 3\sigma(I)$.

^{13}C natural abundance NMR spectra were recorded at 25·2 MHz in a Varian XL-100-15 NMR spectrometer, operating in the FT mode. Chemical shifts are in p.p.m. downfield from internal TMS. ^{13}C spectra were measured as 20% (weight/weight) solutions in chloroform at *ca* 300–303 K.

The structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). From the partial model which was thus obtained, all non-H atoms were located and refined from alternate difference Fourier and isotropic least-squares refinement cycles. After least-squares refinement by full-matrix least squares, based on *F*'s, using anisotropic thermal parameters (*SHELX*76; Sheldrick, 1976), the H atoms were positioned stereochemically. Further refinements were performed with the H atoms riding on bound C atoms; overall temperature factors were refined for the H atoms of the methyl groups, for those of the cyclohexyl ring and for those of benzene ring. The final refinement, with 240 parameters, converged to $R = 0{\cdot}043$, $wR = 0{\cdot}051$; weighting scheme: $w = 3{\cdot}46[\sigma^2(F_o) + 0{\cdot}0003F_o^2]$, maximum shift/e.s.d. = 3×10^{-2}. The residual electron density showed no special features, minimum and maximum values were −0·14 and 0·16 e Å^{-3}, respectively. Scattering factors for H atoms, and scattering factors and anomalous-dispersion corrections for O, C and N were provided in *SHELX*76. Calculations were carried out on a microVAXII system using the programs *SHELX*76, *MULTAN*80, *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1965).

Table 1. *Fractional positional parameters and equivalent isotropic thermal parameters* (Å^2), *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	−0·2503 (1)	0·1992 (2)	0·5083 (1)	3·82 (5)
N(2)	−0·2952 (2)	0·3386 (3)	0·2994 (2)	5·76 (8)
N(3)	0·1025 (2)	0·4766 (2)	0·3586 (2)	4·68 (6)
O(1)	−0·3298 (2)	0·2442 (3)	0·2601 (2)	8·16 (9)
O(2)	−0·3421 (2)	0·4349 (3)	0·2764 (2)	9·1 (1)
O(3)	0·0791 (2)	0·5390 (2)	0·2760 (2)	6·81 (7)
O(4)	0·1989 (1)	0·4744 (2)	0·4136 (1)	6·04 (6)
C(1)	−0·1639 (2)	0·2600 (2)	0·4657 (2)	3·68 (6)
C(2)	−0·1836 (2)	0·3386 (2)	0·3739 (2)	3·95 (7)
C(3)	−0·1002 (2)	0·4104 (2)	0·3398 (2)	4·10 (7)
C(4)	0·0123 (2)	0·4015 (2)	0·3930 (2)	3·92 (6)
C(5)	0·0395 (2)	0·3205 (2)	0·4783 (2)	4·33 (7)
C(6)	−0·0461 (2)	0·2513 (2)	0·5133 (2)	4·40 (7)
C(7)	−0·2290 (2)	0·0850 (2)	0·5668 (2)	5·07 (8)
C(8)	−0·3646 (2)	0·2564 (2)	0·5155 (2)	3·74 (6)
C(9)	−0·3812 (2)	0·2810 (2)	0·6366 (2)	4·28 (7)
C(10)	−0·4945 (2)	0·3475 (2)	0·6427 (2)	5·52 (9)
C(11)	−0·5985 (2)	0·2815 (3)	0·5820 (2)	5·87 (9)
C(12)	−0·5804 (2)	0·2563 (3)	0·4630 (2)	5·90 (9)
C(13)	−0·4681 (2)	0·1867 (2)	0·4570 (2)	5·15 (8)
C(14)	−0·1585 (2)	0·0912 (3)	0·6827 (2)	7·7 (1)
C(15)	−0·1822 (3)	−0·0063 (3)	0·4905 (3)	8·2 (1)

Fractional atomic parameters with equivalent isotropic thermal parameters for the non-H atoms are presented in Table 1. Table 2 shows bond lengths and angles within the molecule and selected intermolecular contacts.* The numbering scheme is shown in Fig. 1.

Discussion. It can be seen in Table 2 that the aromatic ring in the title compound (I) deviates greatly from the ideal symmetry, C_{6mm}, expected for unsubstituted benzene. The endocyclic angle at C(1) is 114·2 (2)°, and this value is similar to the corresponding angle reported for *N*,*N*-diisopropyl-2,4-dinitroaniline (II), 113·7 (2)° (Punte, Rivero, Socolovsky & Nudelman, 1989). The C(1)—C(2) and C(1)—C(6) bond lengths are 1·416 (3) and 1·414 (3) Å, respectively, showing that C—C bonds involving the C atom *ipso* to the amino substituent are longer than the accepted value for benzene, 1·397 Å (Langseth & Stoicheff, 1956, and references therein), and than the mean value for the remaining C—C bonds, 1·375 (6) Å. This feature, together with the enlargement of the endocyclic angles at C(2) and C(6), 124·1 (2) and 122·3 (2)°, respectively, can be explained as being produced by a combination of the electron-releasing properties of the amino group and

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and best least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53565 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Intramolecular bond distances* (Å) *and angles* (°) *and selected intermolecular distances* (Å), *with e.s.d.'s in parentheses*

Bond distances corrected for librational and torsional effects (Maverick & Trueblood, 1988) are in square brackets.

N(1)—C(1)	1·370 (3)	[1·372]	C(3)—C(4)	1·380 (3)	[1·386]
N(1)—C(7)	1·470 (3)	[1·479]	C(4)—C(5)	1·382 (3)	[1·391]
N(1)—C(8)	1·486 (3)	[1·492]	C(5)—C(6)	1·372 (3)	[1·374]
N(2)—O(1)	1·208 (5)	[1·232]	C(7)—C(14)	1·531 (3)	[1·541]
N(2)—O(2)	1·225 (5)	[1·251]	C(7)—C(15)	1·529 (4)	[1·538]
N(2)—C(2)	1·476 (3)	[1·484]	C(8)—C(9)	1·534 (3)	[1·541]
N(3)—O(3)	1·223 (3)	[1·247]	C(8)—C(13)	1·526 (3)	[1·533]
N(3)—O(4)	1·223 (3)	[1·246]	C(9)—C(10)	1·522 (3)	[1·528]
N(3)—C(4)	1·448 (3)	[1·450]	C(10)—C(11)	1·519 (4)	[1·526]
C(1)—C(2)	1·416 (3)	[1·424]	C(11)—C(12)	1·515 (4)	[1·522]
C(1)—C(6)	1·414 (3)	[1·420]	C(12)—C(13)	1·529 (4)	[1·535]
C(2)—C(3)	1·366 (3)	[1·368]			

C(1)—N(1)—C(7)	122·2 (2)	C(1)—C(2)—C(3)	124·1 (2)
C(1)—N(1)—C(8)	120·7 (2)	C(2)—C(3)—C(4)	118·7 (2)
C(7)—N(1)—C(8)	116·2 (2)	N(3)—C(4)—C(3)	119·8 (2)
O(1)—N(2)—O(2)	124·7 (3)	N(3)—C(4)—C(5)	119·9 (2)
O(1)—N(2)—C(2)	117·3 (3)	C(3)—C(4)—C(5)	120·3 (2)
O(2)—N(2)—C(2)	117·7 (3)	C(4)—C(5)—C(6)	120·2 (2)
O(3)—N(3)—O(4)	123·0 (2)	C(1)—C(6)—C(5)	122·3 (2)
O(3)—N(3)—C(4)	118·7 (2)	C(14)—C(7)—C(15)	113·5 (2)
O(4)—N(3)—C(4)	118·3 (2)	C(9)—C(8)—C(13)	110·2 (2)
N(1)—C(1)—C(2)	124·0 (2)	C(8)—C(9)—C(10)	110·8 (2)
N(1)—C(1)—C(6)	121·8 (2)	C(9)—C(10)—C(11)	111·8 (2)
C(2)—C(1)—C(6)	114·2 (2)	C(10)—C(11)—C(12)	110·5 (2)
N(2)—C(2)—C(1)	121·2 (2)	C(11)—C(12)—C(13)	111·7 (2)
N(2)—C(2)—C(3)	114·4 (2)	C(8)—C(13)—C(12)	109·8 (2)

O(2)···C(10^{i})	3·320 (3)	O(4)···C(9^{iii})	3·568 (3)
O(2)···C(15^{ii})	3·336 (2)	O(4)···C(12^{iv})	3·520 (3)
O(3)···C(13^{ii})	3·381 (3)	O(4)···C(14^{v})	3·515 (3)
O(3)···C(6^{iii})	3·528 (3)	C(4)···C(4^{iii})	3·453 (5)
O(4)···C(1^{iii})	3·370 (3)	C(4)···C(5^{iii})	3·576 (3)
O(4)···C(2^{iii})	3·349 (3)	N(3)···C(5^{iii})	3·564 (3)
O(4)···C(3^{iii})	3·588 (3)	N(3)···C(6^{iii})	3·528 (3)

Symmetry code: (i) $-1-x, 1-y, 1-z$; (ii) $-0{\cdot}5-x, 0{\cdot}5+y, 0{\cdot}5-z$; (iii) $-x, 1-y, 1-z$; (iv) $1+x, y, z$; (v) $0{\cdot}5+x, 0{\cdot}5-y, -0{\cdot}5+z$.

electron withdrawal by the 2-nitro group (Domenicano, Vaciago & Coulson, 1975).

The benzene ring is not planar, and its lack of planarity can be seen from the χ^2 value for the best least-squares plane ($\chi^2 = 561$); the deviations of C(1) and C(2) from the mean plane, −0·033 (2) and 0·303 (2) Å, respectively, are probably due to the important *ortho* effect observed. This forces the amino and *o*-nitro groups out of the mean ring plane, the twist angles being $\varphi_1 = 34{\cdot}6$ (5) and $\varphi_2 = 54{\cdot}3$ (5)°, respectively. The τ_1 = C(8)—N(1)—C(1)—C(2) and τ_2 = C(7)—N(1)—C(1)—C(6) torsion angles are −38·4 (3) and −29·0 (3), respectively. These figures are larger than the corresponding ones reported for (II) (Punte *et al.*, 1989) [$\varphi_1 = 30{\cdot}4$ (5), $\varphi_2 = 42{\cdot}5$ (5), $\tau_1 = -30{\cdot}8$ (5) and $\tau_2 = -22{\cdot}8$ (5)°].

The atoms N(1) and N(2) exhibit a pyramidal arrangement, and their distances to the plane defined by their substituents are 0·079 (1) and 0·030 (2) Å, respectively. These N atoms also display deviations from the mean phenyl plane.* The angles formed by the C(1)—N(1) and C(2)—N(2) bonds with the mean ring plane, 5·4 and 10·04°, respectively, are of the order of the values found in (II), 6·5 and 11·25°, respectively (Punte *et al.*, 1989) and are consistent with the *ortho* effect mentioned above.

Both substituents attached to the amine nitrogen have important steric requirements. However, *F*-strain effects are smaller when the atoms are constrained in a ring [the importance of steric and strain effects on amine basicities have recently been emphasized by Alder (1989)]. Therefore, the isopropyl group is situated *anti* to the *ortho* substituent.

The cyclohexane ring, almost perpendicular to the amino group,* adopts a chair conformation with torsion angles ranging from ±54·87 to ±58·03°;* the mean, 56·5 (1·2)°, is larger than the expected value for an ideal chair conformation, 55° (Bucourt & Hainaut, 1965). The C(sp^3)—C(sp^3) bond distances (see Table 2) are in the range 1·515 (4)–1·534 (3) Å, mean 1·526 (7) Å, and the cyclohexane ring angles are in the range 109·8 (2)–111·8 (2)°; the mean, 110·8 (7)°, is slightly smaller than the expected value for an ideal chair conformation, 111·5° (Bucourt & Hainaut, 1965).

The C(1)—N(1) bond length, 1·370 (3) Å, suggests some double-bond character. This length is analogous to that found in *N*,*N*-dimethyl-*p*-nitroaniline, 1·372 (16) Å (Mak & Trotter, 1965), 2,4-dinitroaniline, 1·352 (6) Å (Prasad, Gabe & LePage, 1982) and *N*,*N*-diethyl-4-nitroaniline, 1·351 (4) and 1·354 (4) Å (Maurin & Krygowsky, 1988).

The dihedral angle between the phenyl plane and the *p*-nitro group, 6·5 (2)°, and the C(4)—N(3) bond length, 1·448 (3) Å, are similar to those reported for (II), 5·5 (5)° and 1·450 (3) Å (Punte *et al.*, 1989).

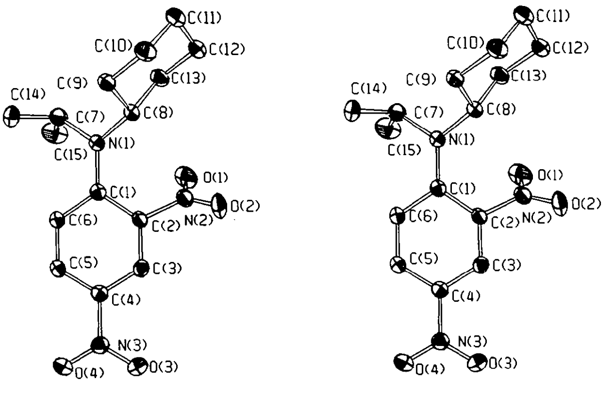

Fig. 1. *ORTEP* drawing, with thermal ellipsoids (20% probability level), showing the atom labelling; non-H atoms included.

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* See deposition footnote.

Valence bond distances and angles displayed by the NO_2 groups in the present compound compare well with the values reported in the literature for other nitro-aromatic compounds (Panunto *et al.*, 1987; Nyburg, Faerman, Prasad, Palleros & Nudelman, 1987). The high thermal parameters shown by the atoms belonging to the *o*-nitro group suggest that this group undergoes a torsional vibration about its C—N bond. Thermal-motion analysis performed using *THMA*11 (Maverick & Trueblood, 1988) supports this assumption. Large-amplitude torsional vibrations and positional disorder have been observed in substituted and unsubstituted nitro-aromatic compounds (Trueblood, Goldish & Donohue, 1961; Nyburg *et al.*, 1987; Domenicano, Schultz, Hargittai, Colapietro, Portalone, George & Bock, 1990).

Effects of substituents on the geometry

The non-additivity of substituent effects on benzene ring geometry has been analyzed using the Domenicano & Murray Rust (1979) (DMR) and Norrestam & Schepper (1981) (NS) angular parameters. Experimental and predicted values are shown in Table 3. Since the angular parameters of the isopropylcyclohexylamino group were not available, dimethylamino-group parameters were used instead. The DMR model tested with the title compound shows non-additivity, the non-additivity parameter (NAP) being 5·9°. NAP is defined as $\text{NAP} = \sum|\theta_i - \theta_i(\text{calc})|$, where θ_i are the endocyclic angles (Krygowsky, 1990, and references therein). The inclusion of NS parameters of highly twisted NO_2 groups for the o-NO_2 substituent, and DMR parameters for the other substituents gives an even greater non-additivity, NAP = 7·6°. The NAP values obtained using both models are greater than 3σ, where $\sigma = [(0{\cdot}2)^2 \times 6]^{1/2} = 0{\cdot}49°$, and therefore indicate interaction between the substituents.

After Krygowsky (1990, and references therein), the departure from the additivity model can be explained as being due to (i) repulsive steric interactions and (ii) strong resonance effects.

In the present study, the *ortho* effect already described also manifests itself in the enlargement of the exocyclic angles N(2)—C(2)—C(1) and N(1)—C(1)—C(2). Therefore, the repulsive deformation parameter (RDP) (Krygowsky, 1990), 4·9°, is greater than 3σ, 1·2°. Hence, the addition of N(2)—C(2)—C(1) and C(2)—C(1)—N(1) angles is larger than could be expected if no steric effects were operating between the amino and *o*-nitro groups, and consequently θ_1 and θ_2 values must be smaller than the predicted values (see Table 3).

Table 3. *Experimental and predicted values for endocyclic bond angles* (°), *with e.s.d.'s in parentheses*

	DMR	DMR*	Exp.
θ_1	116·1 (6)	114·9 (6)	114·1 (2)
θ_2	123·8 (6)	125·5 (5)	123·9 (2)
θ_3	117·6 (5)	116·4 (4)	118·9 (2)
θ_4	121·5 (6)	121·2 (6)	120·0 (2)
θ_5	119·9 (6)	121·1 (5)	120·2 (2)
θ_6	121·2 (5)	120·9 (4)	122·7 (2)

* Twist NO_2 NS parameters for the *o*-nitro substituent.

Regarding resonance effects, it must be noted that in spite of the severe steric effects between the dialkyl-substituted amino and *o*-nitro groups (which turn both substituents out of the phenyl plane, thus leading to deconjugation), several factors point to the existence of a certain degree of conjugation. The analysis of bond-length distribution after thermal-motion correction (Maverick & Trueblood, 1988) would indicate a contribution of the quinoid structure which may be interpreted as due to a cooperative π-electron effect between the *N*,*N*-dialkyl and p-NO_2 groups. Besides, it is known that the increase in conjugation between the ring and the substituent causes a reduction in the angle *ipso* to the substituent (Domenicano *et al.*, 1990, and references therein). Hence, the reduction of θ_1 and θ_4 from the expected values (see Table 3) is consistent with a certain amount of through conjugation (Domenicano & Murray-Rust, 1979).

Geometrical constraints (Krygowsky, 1990, and references therein) and the lack of planarity of the ring described above might explain the departure of θ_3 and θ_6 from the expected values.

Conformation in solution

The lack of planarity of a series of *N*,*N*-dialkyl-substituted 2,4-dinitroaniline molecules in solution has been inferred from ^{13}C NMR spectral data. In order to examine the magnitude of the influence of steric effects on each aromatic carbon as the size of the substituents on the amino moiety is systematically increased, the ^{13}C NMR data for compounds (I) and (II) and for *N*,*N*-dicyclohexyl-2,4-dinitroaniline (III) are presented in Table 4. The experimental and expected values for *N*,*N*-diethyl-2,4-dinitroaniline (IV) are also included in Table 4. Chemical shifts of (IV) were calculated with the additivity rule of substituent effects (Contreras & Kowalevski, 1974) and compared with experimental values. The comparison reveals differences in the chemical shifts for C(2) ($\Delta\delta = -2{\cdot}46$) and C(3) ($\Delta\delta = +3{\cdot}92$). These differences can be explained as being caused by a rotation of the *o*-nitro group out of the ring plane, which produces an increased shielding on the *ipso* carbon and a decreased screening on the *ortho* carbon. As the size of the *N*-alkyl substituents increases, steric strain may be relieved

Table 4. ^{13}C *NMR spectral data for the aromatic ring carbons of* (I), (II), (III) *and* (IV)

All spectra were recorded in $CDCl_3$; chemical shifts (δ) in p.p.m. are relative to tetramethylsilane as internal reference.

	(IV)		(III)	(I)	(II)
	Calc.*	Exp.	Exp.	Exp.	Exp.
C(1)	148·32	147·94	149·22	148·42	147·86
C(2)	132·12	129·66	140·78	139·59	138·49
C(3)	119·79	123·71	126·40	125·64	123·65
C(4)	135·62	135·32	146·15	144·30	142·58
C(5)	129·62	129·85	127·99	126·29	126·08
C(6)	114·38	113·76	121·94	122·14	122·32

* Calculated after Contreras & Kowalevski (1974, and references therein).

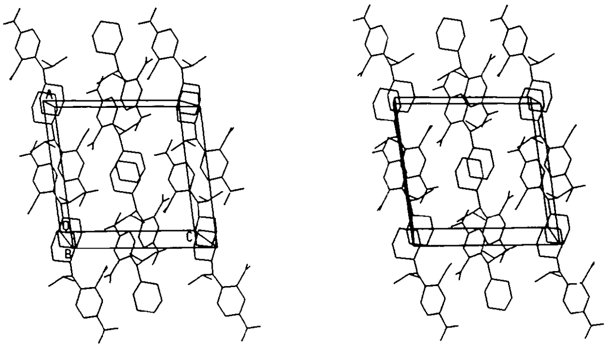

Fig. 2. Stereoscopic view of the molecular packing.

by rotation out of the aromatic plane of either the amino or the nitro moiety so that both groups are partially non-coplanar. The systematic departure from additivity observed for almost all C atoms in (I), (II) and (III) is most likely due to the rotation of both groups.

The reduced shielding effect of the dialkylamino group on C(4) ($\Delta\delta = +10{\cdot}53$, $+8{\cdot}68$ and $+7{\cdot}86$) and on C(6) ($\Delta\delta = +8{\cdot}3$) in (III), (I) and (II), respectively, relative to (IV) indicates the rotation of the NR_2 group. The observed trend would evidence a greater rotation for the *N,N*-dicyclohexyl-substituted compound.

From aromatic ^{13}C shifts it can be inferred that the observed decrease in NR_2 rotation in going from (III) to (II) described above is compensated by an increased rotation of the *o*-nitro group. Consequently, C(2) in (II) is shielded relative to (I) ($\Delta\delta = -1{\cdot}1$) and (III) ($\Delta\delta = -2{\cdot}29$).

^{13}C NMR results reported in Table 4 together with previously reported ^{1}H NMR data (Nudelman *et al.*, 1982) and UV data (Punte *et al.*, 1989) would indicate that *N,N*-dialkyl-substituted 2,4-dinitroaniline molecules in solution have their amino and *o*-nitro groups rotated out of the aromatic ring plane.

X-ray single-crystal studies performed on the three compounds have shown that both the NR_2 and the *o*-nitro groups present important deviations from coplanarity. The values of the twist angles are 34·6 (5) and 54·3 (5)° in compound (I), 28·5 (5) and 40·5 (4)° in compound (II) (Punte *et al.*, 1989), and 37·7 (2) and 37·3 (2)° for molecule *A* and 29·8 (3) and 46·3 (2)° for molecule *B* in compound (III) (Punte & Rivero, 1991). Hence *N,N*-dialkyl-substituted 2,4-dinitroaniline molecules in the solid state present a conformation similar to that inferred from spectroscopic data. Therefore, a trend similar to that found for the molecules in solution when the size of the substituent is increased could be expected. However, a clear tendency was not observed, probably due to intermolecular interactions that cannot be neglected. The influence of packing forces is evidenced through the existence of two crystallographically non-equivalent molecules in compound (III) (Punte & Rivero, 1991).

Molecular packing

A *PLUTO* stereoview of the packing of the molecules in the unit cell is shown in Fig. 2. It can be seen that the molecules are arranged with their long axes oriented approximately along **a**. Assuming van der Waals radii for C, N and O atoms of 1·6, 1·5 and 1·4 Å, respectively, and for CH_2 and CH_3 groups and the half width of the aromatic ring of 1·85, 2·0 and 1·85 Å, respectively (Pauling, 1960), it has been found that some intermolecular distances are smaller than the sum of the corresponding van der Waals radii. These intermolecular contacts (see Table 2) would imply a certain degree of electrostatic contribution to the packing energy. This contribution might be the cause (Panunto *et al.*, 1987; Barzoukas *et al.*, 1987) of the antiparallel coupling of the local dipoles cancelling the second-order crystalline coefficient of the polarizability tensor, thus preventing quadratic nonlinear optical behaviour of the compound in the solid state.

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Structures of an Ylide 4,4,5,5,6,6-Hexafluoro-2-(phenyliodonio)dithianide 1,1,3,3-Tetraoxide (I) and its Complex with Dimethyl Sulfoxide (II)

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Abstract. (I), $C_{10}H_5F_6IO_4S_2$, $M_r = 494{\cdot}2$, monoclinic, $P2_1/n$, $a = 7{\cdot}387\,(3)$, $b = 20{\cdot}403\,(8)$, $c = 10{\cdot}206\,(3)$ Å, $\beta = 99{\cdot}28\,(3)^\circ$, $V = 1518$ Å^3, $Z = 4$, $D_x = 2{\cdot}162$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 24{\cdot}27$ cm^{-1}, $F(000) = 944$, room temperature, final $R = 0{\cdot}073$ for 1757 observed unique reflections. (II), $C_{10}H_5F_6IO_4S_2.C_2H_6OS$, $M_r = 572{\cdot}3$, monoclinic, $P2_1/n$, $a = 8{\cdot}733\,(3)$, $b = 10{\cdot}239\,(2)$, $c = 21{\cdot}101\,(1)$ Å, $\beta = 94{\cdot}47^\circ$, $V = 1881$ Å^3, $Z = 4$, $D_x = 2{\cdot}021$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 20{\cdot}79$ cm^{-1}, $F(000) = 1112$, room temperature, final $R = 0{\cdot}040$ for 2158 observed unique reflections. The crystal structures show that the I atom in both compounds bonds to the methyl C atom of hexafluorodithianide tetraoxide to form an iodonium ylide containing a strong polar bond between the carbanion and the I atom. In (II), the I atom also interacts with the O atom of Me_2SO through charge transfer. The sulfonyl groups with electron deficiency accept electrons from the carbanion by resonance. The resonance delocalizes the negative charge of the carbanion, thereby stabilizing the carbanion and leading to the stable crystallization of the ylide and its complex at room temperature.

Introduction. Phenyliodonium disulfonylmethylides (1), one of the classes of carbene precursors, have aroused great interest because they can react with many kinds of alkenes under a variety of conditions to yield expected products. However, these ylides are difficult to crystallize because of their decomposition at room temperature (Hatjiarapoglou & Varvoglis, 1988), which may be attributed to the instability of the bonding between iodonium and methyl C atoms. Up to now there have been few crystal structure reports about iodonium ylides. As the introduction

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