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

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Abstract. $C_{12}H_{17}N_3O_4$, $M_r = 267{\cdot}3$, monoclinic, $C2/c$, $a = 10{\cdot}059\,(2)$, $b = 12{\cdot}633\,(4)$, $c = 21{\cdot}380\,(5)$ Å, $\beta = 86{\cdot}89\,(2)°$, $V = 2713\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}31$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}93$ cm^{-1}, $F(000) = 1136$, room temperature. Full-matrix least-squares refinement led to final $R = 0{\cdot}049$, $wR = 0{\cdot}058$ for 1319 observed independent reflections. The molecule in the solid state is not planar presenting an extensive rotation of the dialkyl substituted amino and *o*-nitro groups out of the benzene ring [28·5 (5) and 40·5 (4)° respectively]. Additivity of substituent effects on the phenyl shape is analyzed using geometrical parameters proposed by Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283-2286] and Norrestam & Schepper [*Acta Chem. Scand. Ser. A* (1981), **35**, 91–103]. The relationship between the conformation in the solid state, as determined from dihedral angles between the aromatic ring and substituent groups, and that in solution, as inferred from ^{13}C NMR and UV data, is discussed.

Introduction. Derivatives of 2,4- and 2,6-dinitroanilines comprise a group of popular, soil-incorporated, pre-emergence herbicides (Stemmler & Hites, 1987). Most of the leading weed killers are compounds substituted on the amine nitrogen by bulky alkyl groups. Their syntheses, based on the aminodehalogenation of dinitrohalophenyl derivatives, are very difficult, with yields as low as 5% usually obtained (Mann, Jordan & Day, 1968).

In principle, it is reasonable to assume that steric constraints in these types of compounds are so substantial that they make them highly energetic. On the other hand, it has been recently shown that the effect of substituents on the kinetics of the above reaction is not simply that of steric hindrance (Nudelman & Palleros, 1985), and the examination of the structure of some dinitro substrates has been very valuable in interpreting the kinetic results (Nyburg, Faerman, Prasad, Palleros & Nudelman, 1987). The determination of the structure of hindered products can thus yield information regarding the influence of steric hindrance on the molecular geometry and on the packing of the molecules. Since the reactions are carried out in solution it is also of interest to perform additional studies that allow the changes experienced by the compound when it is dissolved in organic solvents to be inferred. To this end we report here the crystal structure analysis of *N*,*N*-diisopropyl-2,4-dinitroaniline together with the examination of its UV and ^{13}C NMR spectra.

Experimental. The title compound was synthesized according to Brady & Cropper (1950) and crystallized by slow evaporation from methanol. A yellowish, irregular-shaped crystal of approximate dimensions 0·15 × 0·25 × 0·4 mm was used for data collection. The measurements were performed on an automatic four-circle Huber diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were obtained from the setting angles of 11 reflections in the range $18{\cdot}5 < 2\theta < 34°$. Systematic absences showed the space group to be $C2/c$ (No. 15). Data were collected in ω scan mode, scan width: 1°, min.–max. scan speed: 0·77–4·62° min^{-1}, to $2\theta_{\max} = 50°$, index range: h $\overline{11}$–11, k 0–14, l $\overline{2}$–25. Three standard reflections ($\overline{2}20$, $13\overline{2}$, $\overline{8}04$), measured every 90 min, showed 5% 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: 2×10^{-3}. No absorption correction was made. From 2887 intensities measured (1706 unique, $R_{\rm int} = 0{\cdot}049$)

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1319 were considered observed using the criterion: $I > 3\sigma(I)$.

The UV spectra were recorded on a Beckman DK2A spectrophotometer. The ^{13}C NMR spectra were obtained on a Varian 100 MHz NMR spectrometer, chemical shifts are referred to TMS.

The structure was solved using direct methods, (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). From the partial model obtained all non-H atoms were located and refined from alternated difference Fourier syntheses 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), a difference electron density synthesis showed the non-methyl H atoms. H atoms belonging to methyl groups were placed at calculated positions. All the H atoms were refined riding on the bonded atoms with two isotropic temperature factors (one for the H atoms belonging to CH_3 and another for the rest). The refinement, with 203 parameters, converged to $R = 0{\cdot}049$, $wR = 0{\cdot}058$, weighting scheme: $w = 1/[\sigma^2(F_o) + 0{\cdot}001789F_o^2]$, maximum shift/e.s.d. = 0·09. The residual electron density showed no special features; min. and max. values were −0·15 and 0·17 e Å^{-3} respectively. Scattering factors and anomalous-dispersion corrections for O, C, N and H were taken from *SHELX*76. Calculations were carried out on a PDP11/34 and on an IBM 4361 using the programs *SHELX*76, *MULTAN*80, *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978).

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

Discussion. Table 2 data show that the benzene ring is severely distorted. Though being aware that "most of the variance in bond angles is related to the electronic properties of the substituents while variance in bond distances can be due to experimental errors" (Domenicano, 1985), both kinds of distortions will be analyzed.

The value of the endocyclic angle at C(1), 113·7 (2)°, considerably less than 120°, is similar to that observed in 2-fluoro-*N*,*N*-dimethyl-4-nitroaniline, 113·8 (4)° (Cox, Hardy, Mackenzie & Macnicol, 1977), 2,6-dinitroaniline, 113·0 (2)° (Párkányi & Kálmán, 1984), *N*,*N*-dimethyl-2,4-

Table 1. *Fractional positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
C(1)	0·7265 (3)	0·0293 (2)	0·0575 (1)	3·7 (1)
C(2)	0·6622 (3)	0·0941 (2)	0·0136 (1)	3·6 (1)
C(3)	0·6722 (3)	0·0761 (3)	−0·0503 (2)	4·0 (1)
C(4)	0·7391 (3)	−0·0112 (3)	−0·0730 (1)	4·1 (1)
C(5)	0·7913 (4)	−0·0830 (3)	−0·0319 (2)	5·2 (1)
C(6)	0·7842 (4)	−0·0633 (3)	0·0309 (2)	5·2 (1)
C(7)	0·7596 (3)	−0·0312 (3)	0·1663 (2)	4·6 (1)
C(8)	0·7415 (3)	0·1622 (2)	0·1425 (1)	4·0 (1)
C(9)	0·6352 (4)	0·1862 (3)	0·1945 (2)	5·7 (2)
C(10)	0·8805 (4)	0·1873 (3)	0·1641 (2)	5·3 (1)
C(11)	0·6513 (5)	−0·1164 (3)	0·1674 (2)	6·8 (2)
C(12)	0·9004 (4)	−0·0784 (3)	0·1644 (2)	6·8 (2)
N(1)	0·7356 (3)	0·0519 (2)	0·1193 (1)	3·79 (9)
N(2)	0·5681 (3)	0·1785 (2)	0·0322 (1)	4·4 (1)
N(3)	0·7464 (3)	−0·0311 (3)	−0·1399 (1)	5·3 (1)
O(1)	0·4926 (2)	0·1639 (2)	0·0781 (1)	5·6 (1)
O(2)	0·5644 (3)	0·2577 (2)	−0·0009 (1)	6·7 (1)
O(3)	0·7032 (4)	0·0365 (3)	−0·1742 (1)	8·0 (1)
O(4)	0·7953 (3)	−0·1141 (2)	−0·1588 (1)	7·1 (1)

* Defined according to Hamilton (1959).

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(2)—C(3)	1·383 (5)	N(2)—O(1)	1·221 (3)
C(2)—C(1)	1·426 (4)	N(3)—O(3)	1·220 (5)
C(2)—N(2)	1·466 (4)	N(3)—O(4)	1·217 (4)
C(3)—C(4)	1·367 (5)	N(1)—C(8)	1·481 (4)
C(4)—C(5)	1·385 (5)	N(1)—C(7)	1·482 (5)
C(4)—N(3)	1·450 (3)	C(8)—C(9)	1·530 (5)
C(5)—C(6)	1·363 (6)	C(8)—C(10)	1·528 (5)
C(6)—C(1)	1·411 (5)	C(7)—C(11)	1·530 (6)
C(1)—N(1)	1·359 (3)	C(7)—C(12)	1·534 (5)
N(2)—O(2)	1·227 (3)		
C(3)—C(2)—C(1)	123·0 (3)	O(2)—N(2)—O(1)	123·3 (3)
C(3)—C(2)—N(2)	113·5 (3)	C(4)—N(3)—O(3)	118·1 (3)
C(1)—C(2)—N(2)	123·2 (2)	C(4)—N(3)—O(4)	118·3 (3)
C(2)—C(3)—C(4)	119·4 (3)	O(3)—N(3)—O(4)	123·6 (3)
C(3)—C(4)—C(5)	119·9 (3)	C(1)—N(1)—C(8)	121·9 (2)
C(3)—C(4)—N(3)	119·2 (3)	C(1)—N(1)—C(7)	122·1 (3)
C(5)—C(4)—N(3)	120·7 (3)	C(8)—N(1)—C(7)	115·4 (2)
C(4)—C(5)—C(6)	120·2 (4)	N(1)—C(8)—C(9)	113·0 (2)
C(5)—C(6)—C(1)	123·1 (4)	N(1)—C(8)—C(10)	110·5 (2)
C(2)—C(1)—C(6)	113·7 (3)	C(9)—C(8)—C(10)	110·7 (3)
C(2)—C(1)—N(1)	125·1 (2)	N(1)—C(7)—C(11)	111·5 (3)
C(6)—C(1)—N(1)	121·2 (3)	N(1)—C(7)—C(12)	116·2 (3)
C(2)—N(2)—O(2)	118·4 (2)	C(11)—C(7)—C(12)	112·4 (3)
C(2)—N(2)—O(1)	118·2 (2)		

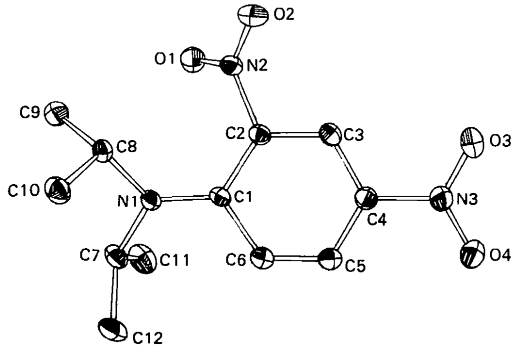

Fig. 1. *ORTEP* drawing, thermal ellipsoids 20%, showing atom labeling of non-H atoms.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and best least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52082 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

dinitro-3-toluidine, 114·6 (2)° (Maurin & Krygowski, 1987) and in other polynitro aromatic compounds such as 2,3,4,6-tetranitroaniline, 114 (4)° (Dickinson, Stewart & Holden, 1966), but smaller than that reported for 2,4-dinitroaniline, 117·9 (4)° (Prasad, Gabe & Le Page, 1982) and for 2,4-dinitroaniline in its 2:1 complex with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), 115·3 (5)° (Weber & Sheldrick, 1981).

The C(1)—C(2) and C(1)—C(6) bond-length values, 1·426 (4) and 1·411 (5) Å respectively, show 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 the mean values for the remaining C—C bonds, 1·375 (9) Å. This feature, as expected for a substituent that causes a decrease in the *ipso* angle (Domenicano, Vaciago & Coulson, 1975), together with an enlargement of the endocyclic angles at C(2) and C(6), 123·0 (3) and 123·1 (4)° respectively, may be explained as being produced by a combination of the electron-releasing property of the amino group and the electron withdrawal by the 2-NO_2 group.

The molecule is not planar: the lack of planarity of the benzene ring can be seen from the χ^2 value for the best least-squares plane ($\chi^2 = 167$). The deviations of C(1) and C(5) atoms from the mean plane defined by the remaining C ring atoms ($\chi^2 = 0·59$), 0·104 and −0·043 Å, are in opposite directions and exceed the limit of 3σ.* There is an extensive rotation of the amino and *o*-nitro groups with respect to the mean ring plane: the twist angles are 28·5 (5) and 40·5 (4)° respectively. These figures are larger than the corresponding ones reported for 2,4-dinitroaniline, 2·7 (5) and 4·3 (4)° respectively (Prasad *et al.*, 1982), and 2,4,6-trinitroaniline, 22·5 and 8·5° for 2-NO_2 and 6-NO_2 respectively (Holden, Dickinson & Bock, 1972). The dihedral angle between the phenyl plane and the *p*-nitro group [5·5 (2)°] corresponds to a C—N bond length, 1·450 (3) Å, shorter than the mean, 1·48 Å, reported by Trotter (1960) for aromatic nitro compounds with non-electron-donating substituents. Notwithstanding, this observed shortening is smaller than the values often quoted in textbooks as evidence for resonance interaction between nitro and aromatic π electrons. Significant deviations from the mean phenyl plane are shown by N(1) and N(2);* these correspond to an inclination of 6·65° for the C(1)—N(1) bond and one of 11·25° for the C(2)—N(2) bond with respect to this plane. These results together with the unequal torsion angles τ_1 = C(8)—N(1)—C(1)—C(2) and τ_2 = C(7)—N(1)—C(1)—C(6), −30·8 (5) and −22·8 (5)° respectively, are consistent with an important *ortho* effect (Fig. 2). As was pointed out earlier by Akopyan, Kitaigorodsky & Struchkov (1965) and Gramaccioli, Destro & Simonetta (1968), these effects are not unusual in overcrowded molecules.

N—O distances, mean 1·221 (4) Å, and O—N—O bond angles, mean 123·4 (2)°, agree with those observed for similar bonds (Holden *et al.*, 1972; Maurin & Krygowski, 1987).

The C(1)—N(1) bond length, 1·359 (3) Å, of the order of that found in *N,N*-dimethyl-*p*-nitroaniline, 1·372 (16) Å (Mak & Trotter, 1965) and 2,4-dinitroaniline, 1·352 (6) Å (Prasad *et al.*, 1982), together with the distribution of bond distances in the ring and the nitro groups, see Table 2, would suggest quinonoid contributions to the overall resonance of the molecule (Holden *et al.*, 1972). Hindrance can explain the rotation of the amino group out of the mean plane and the lengthening of C(1)—N(1) in relation to other aromatic amines with both *ortho*- and *para*-nitro groups (Holden *et al.*, 1972, and references therein).

Geometrical substituent-effects analysis

The comparison of the sequence of endocyclic bond angles in 2,4-dinitroaniline (I) and in the title compound (II) shows significant differences. In order to study these disparities and to establish the influence of substituent effects on valence angles the angular parameters of Domenicano & Murray-Rust (DMR) (1979) and Norrestam & Schepper (NS) (1981) have been used. DMR have suggested that the treatment of substituent effects can be additive and therefore useful for predicting the geometry of polysubstituted benzene rings. They have tested their model with *p*-disubstituted and *m*-trisubstituted compounds but they have made no estimation for *ortho*-disubstituted benzenes where the electronic effects can be greatly altered by the steric effects. NS reported that their treatment can be extended to multisubstituted homo- and heterocyclic aromatic six-membered rings; they have included different angular deformation parameters when the plane of the substituent is twisted out of the ring plane by more than 30°.

Experimental and predicted values for both compounds are shown in Table 3. For compound (I), though the NS model shows a better additivity of

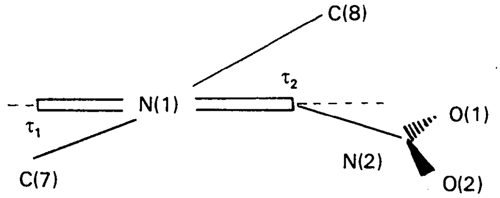

Fig. 2. View down the N(1)—C(1) bond.

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* See deposition footnote.

Table 3. *Endocyclic bond angles* (°) *for* (I), (II) *and* (III)

E.s.d.'s are in parentheses.

	(I)			(II)		
	DMR	NS	Exp.[a]	DMR	DMR*	Exp.
θ_1	117·3 (5)	117·3 (3)	117·9 (4)	116·1 (6)	114·9 (6)	113·7 (3)
θ_2	123·4 (4)	123·3 (4)	122·2 (4)	123·8 (6)	125·5 (5)	123·0 (3)
θ_3	117·2 (3)	117·2 (3)	117·5 (4)	117·6 (5)	116·4 (4)	119·4 (3)
θ_4	121·9 (5)	122·0 (4)	122·3 (4)	121·5 (6)	121·2 (6)	119·9 (3)
θ_5	119·5 (4)	119·3 (4)	121·2 (4)	119·9 (6)	121·1 (5)	120·2 (4)
θ_6	120·8 (3)	120·4 (3)	119·8 (4)	121·2 (5)	120·9 (4)	123·1 (4)

	(III)		
	DMR	NS†	Exp.[b]
θ_1	116·0 (6)	116·6 (6)	113·8 (4)
θ_2	124·3 (5)	123·1 (5)	124·5 (4)
θ_3	117·5 (4)	117·8 (5)	118·9 (4)
θ_4	121·7 (6)	121·9 (7)	120·8 (5)
θ_5	119·1 (5)	119·3 (6)	119·8 (5)
θ_6	121·4 (4)	121·3 (5)	122·7 (4)

References: (*a*) Prasad *et al.* (1982). (*b*) Cox *et al.* (1977).

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

† DMR parameters for the NMe_2 substituent.

angles $[\sum|\theta_i - \theta_i(\text{calc.})|]$, deviations $[\theta_i - \theta_i(\text{calc.})]$ shown by both models are within the 3σ limit. For the case of compound (II), the angular parameters of the diisopropylamino group were not available. Besides, the sequence of endocyclic angles compares fairly well with the values reported by Cox *et al.* (1977) for 2-fluoro-*N*,*N*-dimethyl-4-nitroaniline (III) as can be seen in Table 3; therefore, the dimethylamino group values were used instead. The DMR model used with the title compound (II) data shows a significant non-additivity, $\sum|\theta_i - \theta_i(\text{calc.})| = 9°$. The inclusion of the NS parameter for highly twisted NO_2 groups for the 2-NO_2 substituent with DMR parameters for the other substituents gives an even greater non-additivity, $\sum|\theta_i - \theta_i(\text{calc.})| = 11·1°$. The same order of non-additivity is shown by compound (III) when DMR and NS models are assayed, $\sum|\theta_i - \theta_i(\text{calc.})| = 7·7$ (DMR) and 8·8° (NS). As the appropriate angular parameters have been used in these cases, it can be inferred that the use of the dimethylamino group parameters cannot account for departures of the angles from the predicted values in (II). The common features between the conformations of (II) and (III) are the rotation of the amino group out of the phenyl plane and the deviations of some of the substituent atoms, bound to the ring C atoms, from the mean ring plane. Both effects are probably induced by steric compression.

Solution conformation

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

All spectra were recorded in $CDCl_3$. Chemical shifts relative to tetramethylsilane as internal references.

	(IV)		(II)
	Calc.*	Exp.	Exp.
C(1)	148·5	147·9	147·9
C(2)	132·4	129·7	138·5
C(3)	118·5	123·7	123·7
C(4)	135·9	135·3	142·6
C(5)	129·3	129·9	126·1
C(6)	113·6	113·8	122·3

* Values from Levy & Nelson (1976).

The influence of steric effects in solution has been assessed from the ^{13}C NMR spectrum run in $DCCl_3$; data are shown in Table 4. In order to examine the magnitude of the effect on each carbon, the expected values for *N*,*N*-diethyl-2,4-dinitroaniline (IV), for which parameters are available, were calculated on the basis of an additive treatment. Therefore, expected and experimental values for (IV) have been included in Table 4. Examination of both sets of values reveals differences in the chemical shifts for C(2) ($\Delta\delta = -2·5$) and C(3) ($\Delta\delta = +5$). Those 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 of the *ipso* carbon and a decreased screening of the *ortho* carbon. As the size of the *N*-alkyl substituents increases, steric strain may be relieved by rotation out of the aromatic plane of either the R_2N or the 2-NO_2 group so that both groups are partially non-coplanar. The reduced shielding effect of the dialkylamino group on C(4) and C(6) in (II) compared to that found in (IV) ($\Delta\delta = +6·5$ and $+8·5$ respectively) reflexes the rotation of the R_2N group. Increased rotation of the nitro group in (II) relative to (IV) is evidenced by the upfield shift of C(5) for (II). The fact that the amino and *o*-nitro groups share the necessary twist to relieve the steric compression in *ortho*-nitro tertiary anilines has been previously analyzed on the grounds of ^1H NMR results (Nudelman, Socolovsky & De Waisbaum, 1982).

The lack of planarity of the *ortho*-substituent with the aromatic ring in solution can also be inferred from UV spectra. In fact, the UV spectrum of 2,4-dinitroaniline in methanol shows two bands: band 1 due to the $^+H_2N{=}C(1)\rightarrow C(4){=}NO_2^-$ transition ($\lambda_{max} = 336$ nm, $\varepsilon = 14\,450$) and band 2 due to the $^+H_2N{=}C(1)\rightarrow C(2){=}NO_2^-$ transition [$\lambda_{max} = 390$ nm (sh), $\varepsilon = 6460$]. *N*-Monoalkyl substituted 2,4-dinitroanilines also show two bands. Indeed *N*-methyl- and *N*-ethyl-2,4-dinitroaniline UV spectra are very similar [band 1: $\lambda_{max} = 348$ nm, $\varepsilon = 16\,200$; band 2: $\lambda_{max} = 415$ nm (sh), $\varepsilon = 6300$–6400]. Thus, the effect of monoalkylation on band 1 results primarily from electronic and hydrogen-bonding factors and shows no steric enhancement of resonance. This is reasonable since *N*-monoalkyl substituted 2,4-dinitroanilines take the preferred *s-trans* conformation (Nudelman *et al.*, 1982). Band 2 shows no decreased intensity relative to that of 2,4-dinitroaniline such as would be expected if there were steric inhibition of $^{+}R\mathrm{HN{=}C(1){\rightarrow}C(2){=}NO_2^-}$ resonance.

In going from 2,4-dinitroaniline to *N*,*N*-dimethyl or *N*,*N*-diethyl-2,4-dinitroanilines, a pronounced steric inhibition of $^{+}R_2\mathrm{N{=}C(1){\rightarrow}C(2){=}NO_2^-}$ resonance and a steric enhancement of $^{+}R_2\mathrm{N{=}C(1){\rightarrow}C(4){=}NO_2^-}$ resonance would be expected if the mesomeric electron-withdrawing substituent at C(2) were forced from coplanarity. This expectation is confirmed by the spectral bathochromic displacements of band 1 ($\lambda_{\max} = 368$ and 375 nm respectively) with $\varepsilon = 16\,980$ for both compounds and, furthermore, by the corresponding values for the title compound (II) ($\lambda_{\max} = 380$ nm, $\varepsilon = 10\,000$). This "steric enhancement of resonance" has been fully described (Kamlet, Adolph & Hoffsommer, 1964). The steric inhibition of $^{+}R_2\mathrm{N{=}C(1){\rightarrow}C(2){=}NO_2^-}$ resonance is so strong that not even an inflection marks the position of that electronic transition. In the case of *N*,*N*-diisopropyl-2,6-dinitroaniline (Socolovsky & Nudelman, 1987), the loss of resonance is so important that only a weak band ($\varepsilon = 800$) at 300 nm is observed.

In summary, NMR and UV data indicate that the molecule in solution presents the amino and *ortho*-nitro groups rotated out of the mean ring plane in coincidence with solid-state results.

Molecular packing

It has been recently recognized that molecular complexes may play a catalytic role in chemical transformations (Jencks, 1981; Cattana, Singh, & Anunziata & Silber, 1987). As the title compound possesses conveniently located electron-donor as well as electron-acceptor substituents, examination of its crystal packing may yield information on the degree of electron-donor–acceptor interactions in the presence of steric constraints.

A stereoscopic view of the crystal packing is shown in Fig. 3. It can be seen that the molecules are approximately oriented along **c** forming slabs, centered at $z = 0{\cdot}0$ and $z = 0{\cdot}5$, parallel to the (001) plane. Within each slab the molecules are arranged in layers coincident with their mean ring planes. The existence of interlayer interactions, as induction or charge-transfer effects, can be judged not by interlayer distances but by specific mutual arrangement of the components (Kitaigorodsky, 1984). In the title compound the molecules belonging to consecutive layers display only a partial overlapping of their donor, N^{i}Pr$_2$, and acceptor, *p*-NO$_2$, groups. The size of the alkyl substituents and the hindrance effects that force the amino and *ortho*-nitro groups out of the mean ring plane obstruct the complete opposition of donor and acceptor groups.

Table 5. *Intermolecular contacts shorter than* 3·6 Å

$O(1)\cdots N(3^{i})$	3·161 (4) Å	$O(3)\cdots C(7^{iv})$	3·427 (5) Å
$O(1)\cdots O(4^{i})$	3·349 (4)	$O(3)\cdots C(10^{iii})$	3·593 (5)
$O(2)\cdots C(5^{ii})$	3·498 (5)	$O(3)\cdots C(11^{iv})$	3·599 (5)
$O(2)\cdots C(1^{iii})$	3·573 (4)	$O(4)\cdots C(11^{v})$	3·450 (5)
$O(2)\cdots C(10^{iii})$	3·571 (5)		

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

Adjacent slabs present their layers rotated approximately 60°. This rotation allows a closer approach of donor and acceptor groups along **c**, diminishing voids in the packing and leading to the formation of chains along the above-mentioned direction.

Table 5 shows the shortest intermolecular distances; these would suggest some electrostatic contribution to the packing energy. The C(5)—H(5)···O(2) contact might be the cause of C(5) deviating from the mean ring plane.

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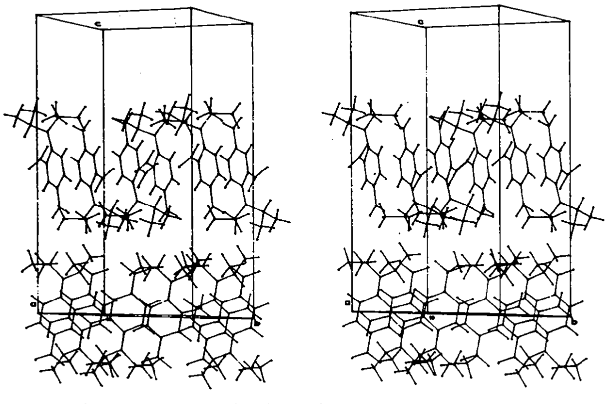

Fig. 3. Stereoscopic view of the molecular packing.

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Structure of 1,1-Dichloro-2,2-bis(4-dimethylaminophenyl)ethylene

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Abstract. $C_{18}H_{20}Cl_2N_2$, $M_r = 335{\cdot}27$, monoclinic, $P2_1/c$, $a = 8{\cdot}091\,(4)$, $b = 6{\cdot}145\,(2)$, $c = 34{\cdot}384\,(10)$ Å, $\beta = 91{\cdot}50\,(3)°$, $V = 1709\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}310$, $D_x = 1{\cdot}303$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}38$ mm^{-1}, $F(000) = 704$, $T = 297$ K, $R = 0{\cdot}046$ for 1053 observed reflections. The C—C ethylene bond distance is 1·328 (11) Å. The twist about the ethylenic bond is 7·1 (5)°. The C—Cl distances are 1·731 (9) and 1·743 (8) Å. One phenyl ring is planar and the other has an approximate boat conformation with a pseudo mirror plane.

Introduction. DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene] is a stable primary degradation product of the important wide-spectrum insecticide DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane].

The X-ray structual study of the present compound, a structural analogue of DDE, was undertaken to provide additional stereochemical information and to study the effects of substitution on the ethylenic bond and the twist about this bond.

Experimental. Transparent, slightly yellowish needle-shaped crystals from alcohol, density by flotation (benzene–bromoform), space group $P2_1/c$, crystal 0·14 × 0·24 × 0·55 mm; cell parameters determined by least squares from setting angles of 15 reflections, $10 \le 2\theta \le 15°$, intensity data measured on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation, 3550 unique reflections collected (*h*

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