Crystal Structure and Molecular Orbital Calculations of *trans*-1-(2-Chloro-4-dimethylaminophenyl)-2-nitroethylene

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The crystal and molecular structure of the title compound has been determined by three-dimensional *X*-ray methods and refined to *R* 0·091 for 1512 independent reflections. The crystals are monoclinic *a* = 7·44, *b* = 7·62, *c* = 19·71 Å, β = 96·0°, space group $P2_1/c$ and *Z* = 4. The atoms in the molecule are practically coplanar. The bond distances indicate that the π electron systems of the anilino, olefinic, and nitro groups are essentially isolated. These findings are confirmed by molecular orbital calculations on the Pariser–Pople–Parr approach. In the crystal lattice the molecules pack plane-to-plane in pairs about centres of symmetry in stacks in the zone of the *b* axis. The short interplanar separation is 3·47 Å.

NITRO-OLEFINS[1] are of some synthetic importance and are known to possess significant biological properties. Several theoretical studies[1-3] have been made of the electronic characteristics of nitro-containing systems but the major emphasis has been placed on the interpretation of the u.v. spectra of nitroaromatic compounds. The molecular structure of nitroethylene has been determined from electron diffraction measurements[4] and its electronic structure investigated using various theoretical approaches.[5,6] So far no structural or theoretical studies have been made of the related arylnitroethylenes which are intermediate between olefinic and aromatic nitro-systems. Such nitrostyrenes with strongly electron-donating substituents exhibit[7] distinctive u.v. absorption and fluorescence characteristics, which are partly the result of the highly dipolar nature of the ground and excited electronic states. It was of interest therefore to obtain direct structural evidence of the overall electronic configuration and the extent of the intramolecular charge transfer for a nitrostyrene system.

EXPERIMENTAL

The title compound was prepared[8] in good yield from the condensation of nitromethane with 2-chloro-4-dimethylaminobenzaldehyde in the presence of n-butylamine.

Crystal Data.—$C_{10}H_{11}ClN_2O_2$, $M = 226{\cdot}6$. Monoclinic, $a = 7{\cdot}44 \pm 0{\cdot}01$, $b = 7{\cdot}62 \pm 0{\cdot}01$, $c = 19{\cdot}71 \pm 0{\cdot}02$ Å, $\beta = 96{\cdot}0 \pm 0{\cdot}1°$, $U = 1111{\cdot}3$ Å^3, $D_m = 1{\cdot}370$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1{\cdot}400$ g cm^{-3}. Cu-K_α radiation $\lambda = 1{\cdot}54178$ Å, $\mu = 30{\cdot}28$ cm^{-1}. Space group $P2_1/c$ (C^5_{2h}, No. 14). The intensities of 1512 independent reflections were estimated visually from equi-inclination Weissenberg photographs (*h*0*l*—*h*6*l*) and for scaling purposes (0*kl*—1*kl*). The measurements were corrected for the Lorentz and polarisation effects but not for absorption, and scaled to the intersecting layers taken about the *a* axis. From a three-dimensional Patterson function sharpened to point atoms at rest (for an overall isotopic temperature factor $B = 3$) a tentative position was assigned to the chlorine atom in space group $P2_1/c$. A three-dimensional Fourier series phased on the position of this chlorine atom clearly indicated the locations of all the light atoms.

The trial structure was refined by the method of least squares with the block diagonal approximation to the normal matrix.

After four cycles with isotropic temperature factors and a weighting function $w = [1 + (||F_0| - 12{\cdot}0|)/10{\cdot}0]^{-1}$ convergence was reached at *R* 0·13. Positions were derived for the hydrogen atoms with locations defined by the molecule structure, the hydrogen atoms were given temperature factors $B = 4$, and subsequently neither these positions nor the temperature factors were refined. The refinement was continued with anisotropic temperature factors on the other atoms, with the weighting function unchanged and after three cycles converged at *R* 0·104. A difference Fourier synthesis was then calculated which showed the positions of the hydrogen atoms of the two methyl groups; when these were included with the other hydrogen atoms, the refinement converged at *R* 0·091.

The observed structure amplitudes and structure factors calculated from the atomic parameters in Table 1 are listed in Supplementary Publication No. SUP 20973 (8 pp.).† All calculations were carried out on the New University of Ulster ICL 1903A computer with programs of the N.U.U. crystal system.[9] Atomic scattering amplitudes were those for neutral atoms given in ref. 10 and the chlorine amplitudes were corrected for the real part of the anomalous dispersion.

The crystal structure projected down the *b* axis is shown in Figure 1, the atomic numbering sequence in Figure 2, and the interatomic distances and interbond angles are given in Table 2.

The crystal is built from stacks of the molecules in the zone of the *b* axis with a centre of symmetry between each pair of molecules in the stack. The separation between the least squares best planes through the molecules is 3·47 Å and the projection perpendicular to a pair of these planes is shown in Figure 3. In the molecule the Cl(1)–C(1) and C(3)–N(1) bonds are inclined at an angle of 16 and 8° respectively to the (010) plane, so that along the *c* axis the planes through molecules in adjacent stacks form an obtuse ' herring bone ' pattern.

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† See note about Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

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TABLE 1

Final atomic parameters * ($\times 10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	2726(3)	3816(1)	5560(1)	205	181	15	−6	2	−8
C(1)	1528(12)	3175(4)	4770(4)	165	107	14	−27	7	22
C(2)	2446(13)	3447(4)	4193(4)	170	120	30	−13	21	−48
C(3)	1661(13)	2909(4)	3540(4)	224	135	17	−8	18	−11
C(4)	−102(13)	2088(4)	3510(4)	192	178	26	−57	31	−33
C(5)	−960(13)	1857(5)	4100(5)	163	139	35	−19	10	−5
C(6)	−185(13)	2393(4)	4772(4)	202	103	19	2	5	33
C(11)	1769(14)	2364(4)	2289(4)	220	339	17	−43	43	−19
C(12)	4319(18)	3946(5)	2988(5)	311	346	23	−12	57	−229
C(21)	−1123(12)	2169(4)	5392(4)	153	123	23	11	50	63
C(22)	−2687(13)	1349(4)	5437(4)	202	185	21	10	50	55
N(1)	2504(11)	3159(3)	2963(3)	216	200	21	−10	22	−27
N(2)	−3460(11)	1165(3)	6099(3)	193	189	29	12	42	77
O(1)	−2737(11)	1858(3)	6606(3)	317	256	25	−28	59	−145
O(2)	−4880(9)	227(3)	6102(3)	231	231	34	19	16	−28
H(2)	3735	4023	4214						
H(4)	−1281	1520	3321						
H(5)	−2200	1298	4076						
H(21)	−639	2640	5867						
H(22)	−3178	907	4969						
H(111)	791	3105	2009						
H(112)	1608	1075	2352						
H(113)	2787	2708	2004						
H(121)	4751	4862	2704						
H(122)	4726	2828	2725						
H(123)	4921	4050	3474						

* The temperature factor $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$.

π Electron SCF-MO Calculations.—The calculations were made within the Pariser–Pople–Parr (PPP) approximation using a published [11] SCF-MO computer program suitably modified to utilise repulsion integrals derived from a simple [12] Mataga expression. The adopted parameters are given in Table 3 and are similar to those used [3,5] in PPP calculations on other comparable nitro-systems. The dimethylamino-group was treated as one atomic centre of $Z = 2$ with an effective ionisation potential I', chosen by appeal to an empirical correlation [13] of substituent I' with u.v. spectral data and molecular ground state dipole moments for substituted nitro-benzenes and -styrenes. The chlorine parameters were deduced similarly and so permit an empirical allowance for σ electron correlation and polarisation effects. These parameters appear chemically reasonable. From a consideration of the structure of nitroethylene, the carbon–(nitro)nitrogen and the ethylenic carbon–carbon resonance integrals were set at 1·2 and 2·9 eV respectively and the remaining carbon–carbon resonance integrals were set at 2·37 eV.

TABLE 2

Distances (Å), angles (°), and π bond orders

	Observed bond length	π Bond order	Calculated * bond length
Cl(1)–C(1)	1·780(8)	0·166	
C(1)–C(2)	1·402(12)	0·695	1·399
C(1)–C(6)	1·408(13)	0·583	1·422
C(2)–C(3)	1·417(13)	0·580	1·423
C(3)–C(4)	1·449(14)	0·581	1·422
C(3)–N(1)	1·369(12)	0·490	1·377
C(4)–C(5)	1·395(14)	0·689	1·400
C(5)–C(6)	1·447(13)	0·572	1·424
C(6)–C(21)	1·478(12)	0·387	1·452
C(11)–N(1)	1·509(13)		
C(12)–N(1)	1·473(15)		
C(21)–C(22)	1·332(14)	0·891	1·359
C(22)–N(2)	1·486(12)	0·214	1·432
N(2)–O(1)	1·207(11)	0·682	
N(21)–O(2)	1·276(11)	0·686	

Cl(1)–C(1)–C(2)	115·2(6)	C(1)–C(6)–C(21)	123·8(8)
Cl(1)–C(1)–C(6)	119·0(6)	C(5)–C(6)–C(21)	123·1(8)
C(2)–C(1)–C(6)	125·7(8)	C(6)–C(21)–C(22)	126·9(9)
C(1)–C(2)–C(3)	120·2(8)	C(21)–C(22)–N(2)	121·6(8)
C(2)–C(3)–C(4)	116·6(8)	C(3)–N(1)–C(11)	121·3(8)
C(2)–C(3)–N(1)	122·2(8)	C(3)–N(1)–C(12)	121·7(8)
C(4)–C(3)–N(1)	121·2(8)	C(11)–N(1)–C(12)	116·1(8)
C(3)–C(4)–C(5)	120·8(9)	C(22)–N(2)–O(1)	120·4(8)
C(4)–C(5)–C(6)	123·6(9)	C(22)–N(2)–O(2)	117·0(8)
C(1)–C(6)–C(5)	113·0(8)	O(1)–N(2)–O(2)	122·6(8)

* $r_{C(1)C(2)} = 1·541 - P_{12}(0·0204)$ Å, $r_{CN} = 1·475 - P_{CN}(0·200)$ Å.

TABLE 3

Pariser–Pople–Parr parameters (in eV) for 1-(2-chloro-4-dimethylaminophenyl)-2-nitroethylene

I'_N(nitro)	= 27·16	β_{NO}	= −3·05	γ_{ClCl}	= 16·5
I'_N(amino)	= 23·16	β_{CN}(nitro)	= −1·20	γ_{NN}	= 16·50
I'_O	= 18·16	β_{CN}(amino)	= −2·00	γ_{OO}	= 14·50
I'_C	= 11·16	β_{CC}(olefin)	= −2·90	γ_{CO}	= 11·35
I'_{Cl}	= 31·16	β_{CC}	= −2·37	γ_{NO}	= 7·20
				$\gamma_{OO'}$	= 4·80

All other repulsion integrals were derived from the formula $\gamma_{pq} = 14·397/(1·27 + r_{pq})$. Formal nuclear charges Z were taken to be N = 2, O = 1, Cl = 2, C = 1.

Table 2 includes the computed π electron bond orders. The prediction of the relevant bond distances is made on the assumption of a linear relationship between the bond distance and the π electron bond order with limits at $P_{12} = 0$ and $P_{12} = 1$ corresponding to standard single and double bond lengths respectively. The uncertainties in the structural data and computed bond orders do not justify the use of a more complicated formula.

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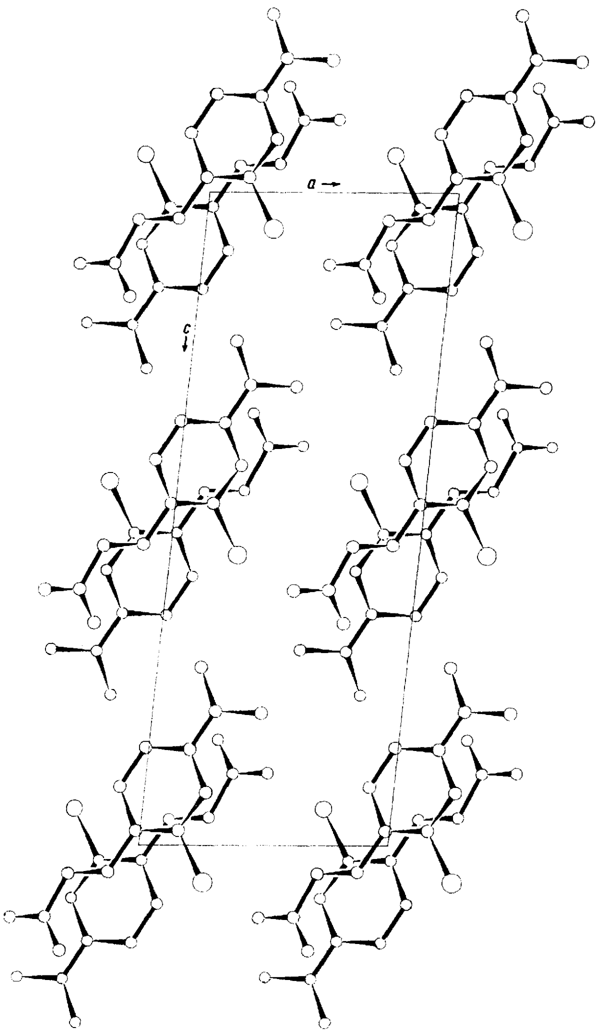

FIGURE 1 Projection of the crystal structure down the *b* axis

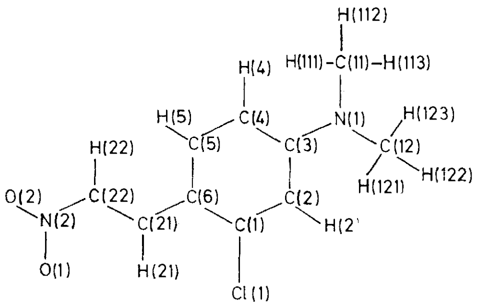

FIGURE 2 Atomic numbering

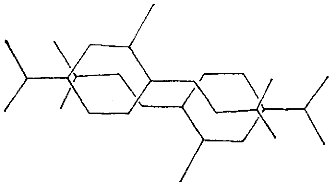

FIGURE 3 Projection of a pair of molecules onto the least squares best plane through atoms C(1)—C(6). The distance between the planes for the two molecules is 3·47 Å

RESULTS AND DISCUSSION

The atoms in the molecule are practically coplanar, their deviations from the least squares best plane through the aryl ring being given in Table 4. The angle between the plane through the atoms C(11), N(1), and C(12) and the least squares best plane through the aryl ring is 3·8°, the torsional angle about the C(6)–C(21) bond between this ring plane and the ethylenic bond C(21)–C(22) is 5·4°, and the torsional angle between the bond C(21)–C(22) and the plane of the nitro-group, O(1), N(2), and O(2), about the C(22)–N(2) bond is also 5·4°. The twist about the three bonds, N(1)–C(3), C(6)–C(21), and C(22)–N(2) is in the same sense with respect to the zone of an axis through atoms C(3) and C(6).

TABLE 4

Deviation from the least squares best plane through atoms C(1)—C(6)

Cl(1)	0·068	C(11)	0·154
C(1)	0·001	C(12)	0·029
C(2)	0·001	C(21)	−0·031
C(3)	−0·001	C(22)	0·058
C(4)	−0·001	N(1)	−0·013
C(5)	0·003	N(2)	0·048
C(6)	−0·003	O(1)	−0·119
		O(2)	0·269

Equation of the plane: $3{\cdot}1039x - 6{\cdot}8499y + 1{\cdot}7597z = -0{\cdot}855$.

The twist about the C(6)–C(21) bond is probably required to relieve the steric repulsion between the hydrogen atoms H(5) and H(22); these two hydrogen atoms are still 2·23 Å apart which is slightly less than a normal Van der Waals contact. Similarly the twist about the C(22)–N(2) bond increase to 2·32 Å the distance between the hydrogen atom H(21) and the oxygen atom O(1).

The essential coplanarity of the nitro-group and the ethylenic function is observed[4] for nitroethylene in the gas phase. The ethylenic–nitro linkage C(22)–N(2) (1·486 Å) compares to 1·475 Å in nitromethane[10] and is a single bond. This length could be the result of a compromise between oxygen–olefinic hydrogen repulsions tending to lengthen and π electron delocalisation effects tending to shorten it; the importance of the latter is indicated both by the small, but finite computed π bond order and by the close adherence to coplanarity of the nitro and olefinic systems.

The ethylenic bond length C(21)–C(22) (1·332 Å) is close to 1·337 Å for an isolated double bond[10] and the high π electron bond order is in good agreement. The bond C(6)–C(22) between the ethylenic and phenyl groups (1·478 Å) is shorter than that 1·53(1) Å found with methyl substituents in a phenyl ring[10] and this again is reflected in the calculated bond order.

The nitrogen atom N(1) of the dimethylamino-group is 0·06 Å from the plane of the three atoms bonded to it. The methyl hydrogen atoms are staggered with respect to an axis between C(11) and C(12). An interaction between the methyl hydrogen atoms H(123) and

H(112) and the two phenyl hydrogen atoms H(2) and H(4) is reduced by a combination of a twist about the bond N(1)–C(3) and the distortion of C(11) from the plane containing atoms C(3), N(1), C(11), and C(12). The carbon–(amino)nitrogen bond C(3)–N(1) is 1·369 Å and is similar to those found in *p*-nitroaniline [14] (1·371 Å) and *NN*-dimethyl-*m*-nitroaniline [15] (1·377 Å); this is much shorter than a carbon–nitrogen single bond length [10] (mean 1·472 Å) so that the formally non-bonding electron pair of the amino-group must be extensively released into the aromatic system. The π electron SCF calculations indicate that considerable charge (+0·251 e) is released from the amino-group, mainly into the aromatic ring (—0·217 e) which can provide suitable acceptor orbitals. The nitro-group, despite its well known ability to function as a strongly electron-withdrawing group, possesses only a nominal excess of electrons, comparable with that on the adjacent ethylenic system. The vacant acceptor π* orbital of the nitro-group lies at too high an energy to perturb the ground-state electron distribution but exerts considerable influence in the excited states. The bonding π orbital of the nitro-group is too low in energy to interact appreciably with the carbon-centred π system and any such interaction involving the non-bonding π orbital of the nitro-group is precluded by a node in the orbital wave function at the nitrogen atom.

The phenyl ring is distorted from a regular hexagon. This is probably a consequence of two factors. The increased orders of the C(3)–N(1) and C(6)–C(21) bonds tends to force a quinonoid structure on the group with a resultant shortening of the C(1)–C(2) and C(4)–C(5) bonds. It should be noted that, despite the formal arrangement of electron acceptor and electron donor groups in a manner suitable for ' quinonoid resonance ' such behaviour is not apparent to any noticeable extent in the molecule as a whole and is only detected in the anilino-system. Secondly the electron-withdrawing chlorine atom will polarise the σ electron density along the C(1)–Cl(1) bond thus reducing the repulsion between the σ electrons of this bond and those of the C(1)–C(2) and C(1)–C(6) bonds so allowing the C(2)–C(1)–C(6) bond angle to open to 125·7°. By a similar argument the electron-donating group bonded at C(3) increases the σ electron density along the bond and causes the C(2)–C(3)–C(4) angle to close to 116·4°; similar distortions have often been observed in substituted phenyl groups.[16,17] The effect of these distorting factors is to leave the bond C(4)–C(5) shorter than the bonds C(3)–C(4) and C(5)–C(6), with the remaining three bonds, affected by both electron-withdrawing and electron-donating groups, accommodating to the distorted bond angles that are required. The nitrogen–oxygen bond lengths of the nitro-group N(2)–O(1) and N(2)–O(2), 1·207 and 1·276 Å, are not equivalent. Oxygen atom O(2) makes short contacts to chlorine (3·37 Å) and to carbon atom C(5) (3·46 Å) in adjacent molecules with the hydrogen atom H(5) close to the direct line between O(2) and C(5). The increased length of the N(2)–O(2) bond therefore could be the result of a weak interaction between atoms O(2), H(5) and O(2), Cl(1). The calculated π electron densities at these atoms (Table 5) supports such a suggestion. A similar disparity in the nitrogen–oxygen bond lengths (1·211 and 1·242 Å) has been reported for *m*-nitroaniline.[18]

TABLE 5

Calculated π electron excess charge densities (× 10^3)

C(1)	43	C(21)	79
C(2)	−78	C(22)	−132
C(3)	2	N(1)	251
C(4)	−89	N(2)	947
C(5)	45	O(1)	−505
C(6)	−140	O(2)	−499
		Cl(1)	75

A negative sign indicates an excess of electronic charge above the formal nuclear charge given in Table 3.

The molecules pack together in a head-to-tail orientation which is expected with a molecular dipole moment of *ca.* 8 D estimated by comparison with 1-(4-dimethylaminophenyl)-2-nitroethylene. The interplanar separation of 3·47 Å is possibly less than a Van der Waals contact and the interaction of the extended dipoles is expected [19] to make only a small contribution to the molecular binding energy.

We thank the N.U.U. Computing Centre for the use of facilities.

[3/2473 *Received*, 3rd *December*, 1973]

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