Crystal Structure of Bis-*p*-nitrophenylcarbodi-imide, $O_2N{\cdot}C_6H_4{\cdot}N{:}C{:}N{\cdot}C_6H_4{\cdot}NO_2$ †

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Crystals of the title compound (I) are orthorhombic with a = 24·738, b = 3·827, c = 13·277 Å, Z = 4, space group $Pna2_1$. The structure was solved by direct methods. 1205 Visually estimated X-ray intensities were refined by full-matrix least-squares to R 7·73%. The molecule differs markedly from an idealised allene type. Important differences (idealised values in parentheses) are: C–N=C 129·6 and 134·4° (120°), N=C=N 169·7° (180°), and C–N · · · N–C torsion angle 113·5° (90°).

THE first accurate structure determination of a carbodi-imide has recently been reported.[1] There are no unexpected features and the molecule has the expected allene-type structure. This is in contrast to the vinylideneamines, containing the C:C:N group, which often show anomalous values for the angle at the nitrogen atom with variations from 123 to 180°.[2-5] Preliminary work on bis-*p*-nitrophenylcarbodi-imide, (I), $O_2N{\cdot}C_6H_4{\cdot}N{:}C{:}N{\cdot}C_6H_4{\cdot}NO_2$, revealed a short axis of length 3·827 Å which suggested that the molecule was either planar or of a distorted allene type.

The presence of nitro-groups in the molecule gave rise to speculation about their interaction with the aromatic rings and the *para*-substituent, in this case the cumulene chain, as observed in some aromatic nitro-compounds. Trotter[6] has reported that C–NO_2 bond lengths in aromatic compounds are *ca.* 1·48 Å, which suggests that there is little evidence for the contribution of quinoidal structures to the resonance hybrid molecule. More recent structure determination of *p*-nitrophenol (1·442 and 1·445 Å in the two crystal forms)[7,8] *p*-nitroaniline (1·460 Å),[9] and *NN*-dimethyl-*p*-nitroaniline (1·405 Å),[10] have suggested that the inclusion of an electron-donating group in addition to the nitro-group results in the quinoidal structure playing a more important role. On the other hand, a recent neutron diffraction study of 1,3,5-trinitrobenzene (two independent molecules)[11] revealed C–NO_2 bond lengths in the range 1·442—1·500 Å so that the criterion of C–NO_2 bond lengths (*vide infra*) is perhaps suspect. The C–NH_2 bond lengths in aromatic amino-compounds are significantly shorter than the C–NO_2 lengths in aromatic nitro-compounds, *e.g. p*-nitroaniline (1·371 Å) and 2-amino-3-methylbenzoic acid (1·367 Å).[12]

EXPERIMENTAL

Crystal Data.—$C_{13}H_8N_4O_4$, M = 284·2. Orthorhombic, a = 24·738(12), b = 3·827(6), c = 13·277(8) Å, U = 1257·0 Å^3, D_m = 1·48, Z = 4, D_c = 1·50, $F(000)$ = 584. Space group $Pna2_1$ or $Pnam$ (from absences), $Pna2_1$ (from statistics). Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 9·8 cm^{-1}.

The preparation of suitable single crystals proved to be difficult as slow conversion into a substituted urea occurred during recrystallisation. Rigorous drying of all solvents proved necessary, and the compound was then reluctant to crystallise by any of the methods used. Eventually several thin plates were obtained by slow evaporation of a solution in 1 : 1 acetone–chloroform. Two crystals were found to be suitable for intensity measurements with dimensions *ca.* 0·06 × 0·56 × 0·48 and 0·10 × 0·26 × 0·30 mm.

Cell dimensions were obtained from oscillation and Weissenberg photographs. Intensities were collected from equi-inclination Weissenberg photographs of the *hk*0—12 and *h*0—3*l* layers and estimated visually. 1215 Independent reflexions were assigned non-zero intensity and were corrected for Lorentz and polarisation effects. Ten of the reflexions were considered to be suitable and necessary for the solution of the structure but not for refinement. Several refixions had bad spot shape and were not estimated. Intensities were placed on the same scale through common reflexions.

Structure Determination and Refinement.—The structure was solved by direct methods using a modified version of the weighted tangent scheme of ref. 13. Table 1(*a*) gives an analysis of the $|E|$ distribution which clearly confirms a non-centrosymmetric space group. Table 1(*b*) gives the starting set of 10 planes and the assigned phases which led to 1024 possible combinations. Three phases were chosen to determine the origin (parity groups *uug*, *guu*, and *gug*) and a fourth plane (parity group *ggg*) to select the enantiomorph. Six other planes were selected so that all parity groups had at least one plane in the starting set. From the 1024 possible combinations 10 were selected on the basis of the lowest reliability index, R_K, generated after one unit-weight cycle of tangent refinement. 10 Cycles of weighted tangent refinement (220 $|E|$ values $>1{\cdot}3$) were then applied to these ten best solutions and final values of R_K calculated in each case. The R_K values ranged from 22·7 to 35·0% with the lowest value not having reached convergence. An E-map calculated with the phases corresponding to the lowest value of R_K revealed positions for all non-hydrogen atoms. Two cycles of full-matrix least-squares refinement (318 planes) with a single isotropic temperature factor reduced R from 22·6 to 12·7%. Refinement with the full data set (1205 planes) and with individual

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† Reprints not available

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TABLE 1

(*a*) $|E|$ Distribution compared with the expected distributions for centro- and non-centro-symmetric structures [14]

	0·0—0·2	0·3—0·8	0·8—2·0	$\langle|E|^2 - 1\rangle$
Centric	0·345	0·213	0·214	0·968
Here	0·227	0·294	0·286	0·749
Acentric	0·181	0·292	0·314	0·736

(*b*) Starting phases used to generate the 1024 possible combinations from which 10 phase sets were chosen for weighted tangent refinement *

Reflexion	$|E|$	Phase	
5 1 0	3·37	0	Origin fixing
4 1 1	2·86	0	
4 1 0	2·36	0	
4 0 12	2·47	$\pi/4$	Enantiomorph
5 2 0	2·32	$0, \pi$	
4 0 11	2·31	$\pi/4, 3\pi/4, -\pi/4, -3\pi/4$	
3 1 11	2·96	$\pi/4, 3\pi/4, -\pi/4, -3\pi/4$	
9 2 1	2·20	$\pi/4, 3\pi/4, -\pi/4, -3\pi/4$	
1 1 1	1·99	$\pi/4, 3\pi/4, -\pi/4, -3\pi/4$	
4 2 0	2·52	$0, \pi$	

* These phases yielded a set of atomic co-ordinates which were then inverted to give the co-ordinates in Table 2. This inversion was done so that the hand of the present molecule would be consistent with the *p*-tolyl compound.[1] All subsequent calculations have been performed with the co-ordinates given in Table 2.

isotropic thermal factors for carbon, nitrogen, and oxygen reduced *R* to 12·6%. Further refinement was carried out with anisotropic temperature factors and the secondary extinction coefficient as a refinable parameter.[15] At *R* 8·4% phenyl group hydrogen atoms were introduced at calculated positions, new positions being obtained before each subsequent refinement cycle. Further anisotropic refinement of the non-hydrogen atoms with a single thermal factor for each group of phenyl hydrogen atoms produced a final *R* value of 7·73%. The ratio of the final mean shift to σ was 0·007 for all parameters.

The weighting scheme was $w = 1/(2{\cdot}51 + F_o + 0{\cdot}017 F_o^2)$ with the constants chosen from an analysis of the variance.[16] Form factors [17] were used in which the imaginary part was set equal to zero. Friedel's law was assumed in the data reduction, and no attempt was made to determine the absolute configuration.

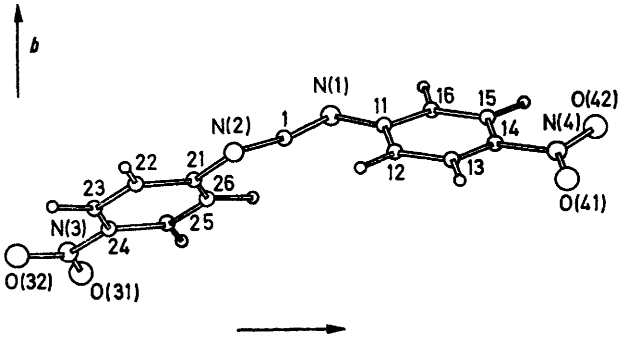

FIGURE 1 Projection of the asymmetric unit down *a* with the labelling of the atoms

RESULTS

The labelling of the atoms is shown in Figure 1 and follows the same scheme as for di-*p*-tolylcarbodi-imide (II).[1]

The final fractional co-ordinates and thermal factors, with estimated standard deviations, are listed in Table 2. The

TABLE 2

(*a*) Final fractional co-ordinates ($\times 10^4$) for the heavier atoms

Atom	x/a	y/b	z/c
N(1)	6116(2)	10,610(16)	2662(6)
N(2)	5969(2)	8430(16)	980(–) *
N(3)	7317(2)	2312(18)	−1905(6)
N(4)	5425(2)	8402(16)	6606(5)
O(31)	7746(2)	1032(18)	−1663(7)
O(32)	7155(3)	2212(27)	−2762(6)
O(41)	5028(2)	6620(19)	6759(6)
O(42)	5676(2)	9867(19)	7278(6)
C(1)	6045(3)	9262(19)	1854(6)
C(11)	5945(2)	9873(16)	3638(6)
C(12)	5448(2)	8300(16)	3824(6)
C(13)	5275(2)	7849(16)	4809(6)
C(14)	5608(2)	8891(14)	5571(6)
C(15)	6102(2)	10,448(17)	5400(6)
C(16)	6270(3)	10,954(18)	4425(6)
C(21)	6319(2)	6756(16)	298(5)
C(22)	6138(2)	6464(17)	−693(6)
C(23)	6473(2)	5037(17)	−1408(7)
C(24)	6973(2)	3819(16)	−1132(6)
C(25)	7150(2)	3992(18)	−146(7)
C(26)	6824(3)	5485(18)	564(6)

* Origin fixed by holding z/c of N(2) constant during refinement.

(*b*) Anisotropic vibrational amplitudes (Å² × 10⁴) †

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	765(35)	598(34)	444(27)	−43(28)	99(25)	−34(28)
N(2)	657(30)	618(33)	410(27)	26(25)	55(23)	11(26)
N(3)	511(26)	703(38)	734(42)	−85(35)	132(27)	20(27)
N(4)	562(28)	641(34)	433(27)	99(27)	25(22)	159(26)
O(31)	667(30)	986(44)	1059(44)	−86(41)	137(32)	286(30)
O(32)	829(37)	1712(77)	678(36)	−438(48)	49(33)	331(44)
O(41)	793(33)	926(44)	644(31)	227(31)	134(26)	−109(31)
O(42)	810(31)	1078(47)	456(26)	−43(32)	−102(23)	31(31)
C(1)	594(33)	550(35)	431(33)	37(29)	96(24)	19(27)
C(11)	633(32)	417(28)	336(24)	−25(25)	31(24)	41(25)
C(12)	543(30)	501(33)	441(30)	−55(27)	−86(25)	−33(26)
C(13)	467(27)	472(29)	435(28)	17(27)	−50(23)	0(25)
C(14)	469(26)	419(27)	352(24)	−19(23)	−33(21)	94(21)
C(15)	521(30)	511(33)	435(30)	−83(27)	−70(23)	26(26)
C(16)	490(27)	507(33)	516(34)	−52(29)	34(25)	−56(25)
C(21)	544(29)	430(28)	362(26)	14(24)	24(23)	−66(23)
C(22)	483(29)	522(34)	424(29)	38(26)	−17(24)	−64(24)
C(23)	513(28)	558(33)	404(27)	−29(26)	1(23)	−21(26)
C(24)	459(25)	450(31)	566(34)	−48(28)	50(25)	−39(22)
C(25)	460(27)	555(35)	628(39)	70(33)	−97(27)	−25(26)
C(26)	558(30)	584(35)	441(29)	−37(32)	−89(26)	−84(28)

† In the form

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots]$$

(*c*) Final fractional co-ordinates ($\times 10^4$) and isotropic vibrational amplitudes (Å² × 10⁴) for the hydrogen atoms. Each atom is assigned the same number as the carbon atom to which it is attached. A single temperature factor was used for the hydrogen atoms of each of the two phenyl groups

Atom	x/a	y/b	z/c	U_{iso}
H(12)	5195	7457	3213	421(108)
H(13)	4888	6656	4962	421(108)
H(15)	6356	11,273	6103	421(108)
H(16)	6654	12,171	4281	421(108)
H(22)	5744	7399	−905	413(108)
H(23)	6338	4865	−2175	413(108)
H(25)	7541	3009	66	413(108)
H(26)	6962	5660	1328	413(108)

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[14] D. Rogers, 'Computing Methods in Crystallography,' Pergamon Press, London, 1965, p. 123.

[15] A. C. Larson, 'Crystallographic Computing,' Munksgaard, Copenhagen, 1970, p. 291.

[16] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, London, 1961, p. 32.

[17] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

thermal factors for oxygen atoms are, as expected, higher than for other atoms. No correction for thermal motion has been applied to the bond lengths and angles. An analysis of the agreement between F_o and F_c is given in Table 3. A similar analysis in terms of parity groups shows that the agreement is less good for groups *ggg* and *ggu* (R 9·65 and 8·46%) than for other groups (6·50—7·40%). This arises from the inclusion of a large number of *h0l* reflexions collected about *c* which had bad shape on all layers. R for 203 *h0l* reflexions is 10·21%. This feature probably accounts for R not showing the normal significant decrease as a function of F_o. Many of the *h0l* reflexions were strong and on average their intensity was higher than the *hkl* reflexions. A Table of observed and calculated structure factors is published in Supplementary Publication No. SUP 20453 (13 pp., 1 microfiche).*

TABLE 3

R as a function of the magnitude of F_o and of sin θ

$10F_o/F_o$(max.) *	No.	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	ΣΔ	R
0·00—0·19	79	149	149	26	17·63
0·19—0·24	97	248	236	33	13·58
0·24—0·29	95	296	287	35	11·96
0·29—0·33	87	322	308	34	10·57
0·33—0·39	98	419	400	47	11·40
0·39—0·46	95	477	465	39	8·25
0·46—0·53	95	561	542	44	7·93
0·53—0·64	95	660	636	55	8·35
0·64—0·78	93	787	758	56	7·20
0·78—0·94	97	986	976	65	6·66
0·94—1·21	91	1150	1138	62	5·43
1·21—1·80	86	1494	1524	109	7·34
1·80—10·0	97	3373	3367	233	6·92
10 sin θ					
0·0—4·2	102	2757	2715	194	7·04
4·2—5·3	120	1861	1847	106	5·73
5·3—6·2	121	1150	1136	86	7·53
6·2—6·8	117	1189	1188	89	7·48
6·8—7·4	127	1088	1079	93	8·61
7·4—7·9	110	807	799	66	8·18
7·9—8·4	128	627	602	57	9·17
8·4—8·9	136	588	580	54	9·34
8·9—9·4	130	520	521	56	10·78
9·4—10·0	114	335	324	39	11·89
All	1205	10,928	10,794	844	7·73

* F_o(max.) = 119·21.

Bond lengths and angles are listed in Table 4. The mean C–C length in the phenyl groups (1·379 Å) is less than the standard value (1·394 Å).[18] This compares with 1·386 Å for di-*p*-tolylcarbodi-imide. The difference between C(1)–N(1) and C(1)–N(2) is not significant ($<2\sigma$). The N(1)–C(11) and N(2)–C(21) lengths (1·392 and 1·406 Å) are very significantly less than the single-bond value (1·475 Å) and, moreover, are significantly less than the equivalent bonds in the tolyl compound (1·428 and 1·432 Å). The C–NO_2 lengths (1·459 and 1·453 Å) are similar to the lengths found in *p*-nitroaniline (1·460 Å, corrected for thermal motion) and *p*-nitrophenyl azide (1·447 Å).[9,19]

The angle at the central carbon atom (169·7°) is similar to that found in other cumulenes [1-5] and probably deviates from 180° as a result of packing forces. The C–C–C angles at the nitro-groups (121·5 and 122·6°) are the largest in each phenyl group, a common feature of aromatic nitro-compounds.[7-11,19] In comparison, the tolyl compound has its largest ring angles at non-substituted carbon atoms. The larger angles assumed by N(1)–C(11)–C(12) and N(2)–C(21)–C(26) (121·4 and 123·3°) than by N(1)–C(11)–C(16) and N(2)–C(21)–C(22) (117·9 and 116·5°) are probably due to the intramolecular contacts of C(12) and C(26) with the cumulene chain. C(16) and C(22) do not have similar contacts. The C–N=C angles (134·4 and 129·6°) are slightly larger than in the tolyl compound (127·2 and 128·4°), both pairs being significantly larger than the idealised allene type value (120°).

TABLE 4

Bond lengths (Å) and angles (°)

(*a*) Distances

C(1)–N(1)	1·203(9)	C(1)–N(2)	1·219(9)
C(11)–N(1)	1·392(8)	C(21)–N(2)	1·406(8)
C(14)–N(4)	1·458(7)	C(24)–N(3)	1·453(8)
O(41)–N(4)	1·211(8)	O(31)–N(3)	1·211(8)
O(42)–N(4)	1·223(8)	O(32)–N(3)	1·206(9)
C(11)–C(12)	1·391(8)	C(21)–C(22)	1·394(8)
C(12)–C(13)	1·386(9)	C(22)–C(23)	1·373(9)
C(13)–C(14)	1·365(8)	C(23)–C(24)	1·373(8)
C(14)–C(15)	1·378(8)	C(24)–C(25)	1·381(9)
C(15)–C(16)	1·373(9)	C(25)–C(26)	1·366(10)
C(16)–C(11)	1·382(9)	C(26)–C(21)	1·387(9)
Mean C(Ph)–C(Ph)	1·379	Mean C(Ph)–C(Ph)	1·379

(*b*) Angles

N(2)–C(1)–N(1) 169·7(8)

C(1)–N(1)–C(11)	134·4(6)	C(1)–N(2)–C(21)	129·6(6)
N(1)–C(11)–C(16)	117·9(6)	N(2)–C(21)–C(22)	116·5(5)
N(1)–C(11)–C(12)	121·4(5)	N(2)–C(21)–C(26)	123·5(5)
N(4)–C(14)–C(13)	118·2(5)	N(3)–C(24)–C(23)	118·3(6)
N(4)–C(14)–C(15)	119·1(5)	N(3)–C(24)–C(25)	120·2(6)
C(14)–N(4)–O(41)	118·9(6)	C(24)–N(3)–O(31)	119·0(7)
C(14)–N(4)–O(42)	118·0(5)	C(24)–N(3)–O(32)	119·0(6)
O(41)–N(4)–O(42)	123·1(6)	O(31)–N(3)–O(32)	121·9(7)
C(11)–C(12)–C(13)	119·6(5)	C(21)–C(22)–C(23)	119·4(5)
C(12)–C(13)–C(14)	118·5(5)	C(22)–C(23)–C(24)	119·6(6)
C(13)–C(14)–C(15)	122·6(5)	C(23)–C(24)–C(25)	121·5(6)
C(14)–C(15)–C(16)	118·9(5)	C(24)–C(25)–C(26)	119·2(6)
C(15)–C(16)–C(11)	119·7(6)	C(25)–C(26)–C(21)	120·2(6)
C(16)–C(11)–C(12)	120·6(5)	C(26)–C(21)–C(22)	120·1(5)

Table 5 gives equations for some least-squares planes and deviations of atoms from these planes. The deviations for planes (1)—(4) are very similar to those found in the tolyl compound. The NO_2 group containing N(3) and the C=N–C chain containing N(2) are much more nearly in the plane of the phenyl group to which they are attached than is the case for the corresponding groups of atoms in the other half of the molecule. This feature is emphasised by the torsion angles given in Table 6 but it does not seem to manifest itself in any large differences in bond lengths in the two halves of the molecule. The torsion angle C(11)–N(1) · · · N(2)–C(21) is 113·5° which is a considerable deviation from that in an idealised allene-type structure (90°). The tolyl compound does not exhibit this feature.

Figure 2 shows the packing of the molecules in the crystal. Due to the short *b* axis, every atom is separated from two identical atoms in this direction by the length of *b* (3·827 Å).

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[18] *Chem. Soc. Special Publ.*, No. 18, 1965.

[19] A. Mugnoli, C. Mariani, and M. Simonetta, *Acta Cryst.*, 1965, **19**, 367.

TABLE 5

Equations of best least-squares planes in the form $Ax + By + Cz = D$ and, in square brackets, distances (Å) of the atoms from the planes

	A	*B*	*C*	*D*
Plane (1): C(11)—(16)	−0·4382	0·8988	−0·0124	−3·1078
[C(11) −0·001, C(12) −0·006, C(13) 0·010, C(14) −0·005, C(15) −0·002, C(16) 0·006]				
Plane (2): C(21)—(26)	0·3964	0·8978	−0·1917	8·4307
[C(21) 0·011, C(22) −0·015, C(23) 0·005, C(24) 0·007, C(25) 0·011, C(26) 0·002]				
Plane (3): C(11)—(16), N(1), C(1)	−0·4470	0·8933	−0·0470	−3·4662
[C(11) 0·040, C(12) 0·040, C(13) 0·016, C(14) −0·044, C(15) −0·047, C(16) 0·001, N(1) 0·164, C(1) −0·168]				
Plane (4): C(1), N(2), C(21)—(26)	0·4082	0·8855	−0·2218	8·6247
[C(1) 0·073, N(2) −0·028, C(21) −0·042, C(22) −0·032, C(23) 0·033, C(24) 0·045, C(25) −0·008, C(26) −0·041]				
Plane (5): O(41), O(42), N(4), C(11)—(16)	−0·4814	0·8758	−0·0352	−3·9461
[O(41) −0·139, O(42) 0·154, N(4) −0·007, C(11) 0·005, C(12) 0·061, C(13) 0·070, C(14) −0·014, C(15) −0·072, C(16) −0·057]				
Plane (6): C(21)—(26), N(3) O(31), O(32)	0·4058	0·8958	−0·1815	8·5759
[C(21) 0·011, C(22) −0·032, C(23) −0·013, C(24) 0·006, C(25) 0·005, C(26) 0·018, N(3) 0·021, O(31) 0·030, O(32) −0·046]				

Several of the shortest contacts shown in Table 7 are due to this purely translational symmetry. No contacts are, however, unduly short. The packing arrangement in the tolyl compound is different in that the closest contacts are between molecules related by two-fold screw axes. The shortest contacts involving oxygen atoms with non-hydrogen atoms involve the oxygen atoms bonded to N(4) (3·09—3·25 Å). The shortest contacts experienced by the oxygen atoms on N(3) are substantially longer [O(32) · · · O(42) 3·77, O(31) · · · N(1) 3·44, and O(31) · · · C(16) 3·40 Å]. This feature can be correlated with the lower thermal factors of O(41) and O(42) compared with O(31) and O(32). The 3·09 Å contact of O(41) is with the central carbon atom C(1): the shortest contact with a carbon atom that is bonded to a hydrogen atom is 3·20 Å. The oxygen atoms are involved in a large number of relatively short intermolecular contacts, but none is short enough to suggest the presence of hydrogen bonding.

TABLE 6

Torsion angles (°)

C(11)–N(1) · · · N(2)–C(21)	113·5
C(1)–N(1)–C(11)–C(12)	31·6
C(1)–N(1)–C(11)–C(16)	27·6
C(1)–N(2)–C(21)–C(22)	6·5
C(1)–N(2)–C(21)–C(26)	5·3
C(13)–C(14)–N(4)–O(41)	11·4
C(15)–C(14)–N(4)–O(42)	11·1
C(23)–C(24)–N(3)–O(32)	0·7
C(25)–C(24)–N(3)–O(31)	4·3

TABLE 7

Intermolecular contacts (Å)

Type		Shortest
O · · · O	O(41) · · · O(42)	3·12 *
O · · · N	O(41) · · · N(1)	3·25
O · · · C	O(41) · · · C(1)	3·09
O · · · H	O(31) · · · H(16)	2·44
N · · · N	N(2) · · · N(1)	3·75 *
N · · · C	N(2) · · · C(21)	3·42 *
N · · · H	N(3) · · · H(26)	3·01
C · · · C	C(11) · · · C(12)	3·46 *
C · · · H	C(22) · · · H(13)	2·94
H · · · H	H(22) · · · H(13)	2·48

* Atoms related by translation in the *b* direction.

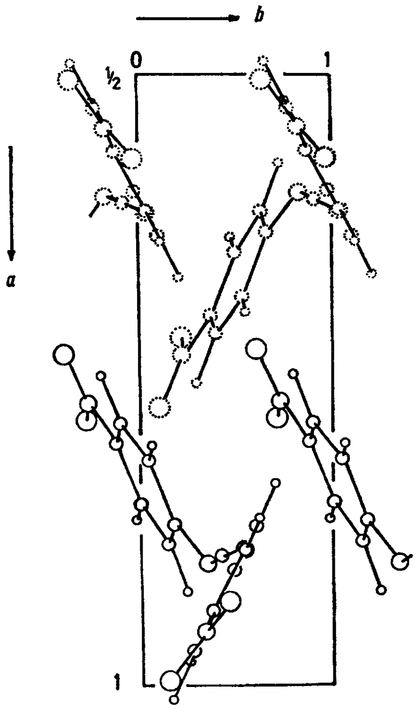

FIGURE 2 Projection of the contents of half the unit cell down *c*

TABLE 8

Summary of equivalent structural features in (I) and (II).[1] Where appropriate, results for (III)[5] have been included [labelling of the atoms is not consistent between (III) and the other two structures]

	(I)	(II)	(III)
(*a*) Bond lengths (Å)			
C(1)–N(1)	1·203	1·223	1·206
C(1)–N(2)	1·219	1·204	
C(11)–N(1)	1·392	1·428	1·427
C(21)–N(2)	1·406	1·432	
Mean C(Ph)–C(Ph)	1·379	1·387	1·382
	1·379	1·385	
(*b*) Bond angles (°)			
N(1)–C(1)–N(2)	169·7	170·4	
C(1)–N(1)–C(11)	134·4	127·2	124·6
C(1)–N(2)–C(21)	129·6	128·4	
(*c*) Torsion angles (°)			
C(11)–N(1) · · · N(2)–C(21)	113·5	88·0	
C(1)–N(1)–C(11)–C(12)	31·6	21·0	2·1
C(1)–N(1)–C(11)–C(16)	27·6	18·6	
C(1)–N(2)–C(21)–C(22)	6·5	7·1	
C(1)–N(2)–C(21)–C(26)	5·3	8·7	

DISCUSSION

The primary objective of this analysis was to determine the relationship between the short *b* axis and the stereochemistry of the molecule. The main structural features is the adoption of a distorted allene-type configuration which allows the molecule to pack with 3·827 Å translational symmetry.

Table 8 compares structural features with equivalent ones in di-*p*-tolylcarbodi-imide (II) and in *N*-*p*-tolyl-2,2-diphenylvinylideneamine (III), $Ph_2C{:}C{:}N{\cdot}C_6H_4Me$. The bond lengths and angles in (II) and (III) are very similar for the half of the molecule which comes closest to being planar [C(1),N(2),C(21)—(26)]. The introduction of a nitro-group appears to have two important effects. The first involves the torsion angle, as discussed earlier. The second is the significant reduction (*ca.* 4σ) in the C(11)–N(1) and C(21)—N(2) bond lengths. The shortening of these bonds could be due to a significant contribution of a quinoidal structure to the hybrid molecule, the lone pairs on the nitrogen being the source of electron donation. A consequence of this would be a change in the N=C=N bonding which can be detected in the deviation from an allene-type structure. However, confirmatory evidence from the C–C bond lengths in the phenyl groups is not so strong, as only one of the aromatic rings [C(21)—(26)] shows a shortening in the 2,3- and 5,6-bonds. Evidence from the $C{-}NO_2$ bond lengths is inconclusive in this respect.

The correlation between N=C lengths and the value of the angle at the nitrogen atom remains consistent with previous results.[1-5]

We thank Dr. G. M. Sheldrick for the use of his computer programmes, the University Computer Laboratory for their facilities, and the S.R.C. for the provision of equipment and for maintenance grant (to A. T. V.).

[2/840 *Received*, 14*th April*, 1972]