Crystal Structure of Di-*p*-tolylcarbodi-imide, $MeC_6H_4{\cdot}N{:}C{:}N{\cdot}C_6H_4Me$ †

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Crystals of the title compound are orthorhombic with $a = 11{\cdot}310$, $b = 14{\cdot}799$, $c = 7{\cdot}690$ Å, $Z = 4$, space group $P2_12_12_1$. 1511 Visually estimated *X*-ray reflexions were refined by least squares to *R* 6·25%; the structure was solved by direct methods. The stereochemistry of the molecule is of the allene type with the two C–N=C planes approximately normal to each other, with C–N=C angles of 127·2(3) and 128·4(3)°, and with an N=C=N angle of 170·4(4)°.

In earlier work, dipole-moment messurements were used to predict the stereochemistry of carbodi-imides $R^1N{:}C{:}NR^2$. Bergmann and Schütz[1] interpreted their results in terms of a linear structure for *NN*′-disubstituted carbodi-imides. However, Schneider[2] suggested that a three-dimensional asymmetrical structure was equally compatible with the observed results. More recently, Feichtmayr and Würstlin[3] have made further dipole-moment measurements and have concluded that carbodi-imides have allene-type structures which should exist as enantiomorphs with the planes containing R^1 and R^2 normal to each other. Vinylideneamines, containing the C:C:N group, often show anomalous values for the angle at the nitrogen atom with variations from 123—180°.[4–7] The structure of di-*p*-tolylcarbodi-imide has been determined to see if the molecule assumed the configuration predicted from classical stereochemistry or shows unpredictable angles as do the vinylideneamines. The only previous structural determination of an *NN*′-disubstituted carbodi-imide had shown the C·N:C:N·C chain to be bent at the nitrogen atoms but no angles were reported as only the *hk*0 projection was solved.[8]

EXPERIMENTAL

Crystal Data.—$C_{15}H_{14}N_2$, $M = 222{\cdot}3$, Orthorhombic, $a = 11{\cdot}310(8)$, $b = 14{\cdot}799(10)$, $c = 7{\cdot}690(7)$ Å, $U = 1287{\cdot}1$ Å^3, $D_m = 1{\cdot}15$, $Z = 4$, $D_c = 1{\cdot}148$, $F(000) = 472$. Space group $P2_12_12_1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu-}K_\alpha) = 5{\cdot}4$ cm^{-1}.

Cell dimensions were obtained from oscillation and Weissenberg photographs and agreed well with values previously determined.[8] Intensities were collected from equi-inclination Weissenberg photographs of the *hk*0—7 and 0—10*kl* layers and estimated visually. The same crystal was used for both sets of measurements. 1511 Independent reflexions were assigned non-zero intensity and were corrected for Lorentz and polarisation effects, but not for absorption. The intensities were placed on the same scale through common reflexions. The 002 reflexion was noted to have the strongest intensity but, due to its diffuseness, a satisfactory intensity measurement could not be made.

Structure Determination and Refinement.—The structure was solved by direct methods. Three phases were chosen to determine the origin (parity groups *guu*, *ggu*, and *ugu*) and a fourth phase (parity group *ggu*, to give a structure invariant) to select the enantiomorph. Two planes were chosen from the parity groups *gug* and *uug*, and the four possible combinations of their phases used as a starting set together with the origin- and enantiomorph-determining phases. Six cycles of least-squares refinement (60 planes) and twelve cycles of tangent refinement (211 planes with $E > 1{\cdot}45$) were used for each of the four starting sets of phases. *E*-maps were calculated in each case from the 211 reflexions with their refined phases. One such map could be interpreted in terms of a partial structure consisting of one phenyl group with substituent atoms in the 1- and 4-positions, and two atoms which appeared to be part of the other phenyl group. A complete structure was derived from this information, and full-matrix least-squares refinement (385 planes) reduced *R* to 15·2% with a single isotropic thermal factor. Refinement was continued with the full data set, with isotropic thermal factors for the nitrogen and carbon atoms, and the secondary extinction coefficient[9] as a refineable parameter. At *R* 12·4% phenyl group hydrogen atoms were introduced at calculated positions, new positions being obtained before each subsequent refinement cycle. Anisotropic refinement of the non-hydrogen atoms with an overall thermal factor for each group of phenyl hydrogen atoms reduced *R* to 7·75%. A difference Fourier synthesis was then calculated in an attempt to locate the methyl hydrogen atoms. Six peaks at chemically reasonable positions were found, but they were somewhat diffuse. Three of the hydrogen atoms refined satisfactorily, but it was necessary to fix the others at stereochemically reasonable positions all of which were within the regions of electron density found on the diffrence map. Further refinement cycles with a fixed thermal factor for the methyl hydrogen atoms yielded a final *R* of 6·25%. The final mean shift to σ ratio was 0·012 for all parameters.

The weighting scheme[10] was $w = 1/(0{\cdot}74 + F_o + 0{\cdot}03F_o^2)$ with the constants chosen from an analysis of the variance. Scattering factors[11] were used in which the imaginary part was set equal to zero. Friedel's law was

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† Reprints not available.

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[9] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.

[10] 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.

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

assumed in the data reduction, and no attempt was made to determine the absolute configuration.

RESULTS

The final fractional co-ordinates, anisotropic and isotropic temperatute factors, with their estimated standard deviations given as units in the last place, are listed in Tables 1 and 2. The thermal factors for the two methyl carbon atoms are considerably higher than for the carbon atoms to which they are attached. No correction for thermal motion has been applied to the bond lengths and angles. An analysis of the agreement between observed and calculated structure factors is given in Table 3. A similar analysis in terms of parity groups shows a very even distribution in terms of both the number of reflexions and the values of R. A Table of observed and calculated structure factors is published in Supplementary Publica-No. SUP 20330 (15 pp., 1 microfiche).* The labelling of the atoms is shown in Figure 1.

TABLE 1

(*a*) Final fractional co-ordinates ($\times 10^4$) for the heavier atoms with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
N(1)	5124(3)	1874(2)	5927(4)
N(2)	4829(2)	474(2)	4364(4)
C(1)	4887(3)	1178(2)	5142(5)
C(11)	4637(3)	2752(3)	5641(5)
C(12)	3556(3)	2881(3)	4795(5)
C(13)	3121(3)	3740(3)	4588(6)
C(14)	3719(3)	4493(3)	5196(5)
C(15)	4782(4)	4353(3)	6062(5)
C(16)	5246(3)	3491(3)	6285(5)
C(17)	3242(6)	5442(3)	4907(8)
C(21)	3971(3)	−231(2)	4539(5)
C(22)	4161(3)	−1031(2)	3635(5)
C(23)	3348(3)	−1724(2)	3747(5)
C(24)	2333(3)	−1634(2)	4774(4)
C(25)	2165(3)	−822(2)	5641(4)
C(26)	2964(3)	−125(2)	5536(4)
C(27)	1441(5)	−2388(3)	4905(7)

(*b*) Final fractional co-ordinates ($\times 10^4$) and isotropic vibrational amplitudes (10^4 Å^2) for the hydrogen atoms. Each atom in a phenyl group is assigned the same number as the carbon atom to which it is attached. Each atom in a methyl group has the same first two numbers as the attached carbon atom. Refined parameters have estimated standand deviations in parentheses. A single temperature factor was used for each group of phenyl hydrogen atoms

Atom	x/a	y/b	z/c	U_{iso}
H(12)	3075	2308	4304	750(69)
H(13)	2302	3834	3936	750(69)
H(15)	3363	5173	5016	750(69)
H(16)	5251	4923	6555	750(69)
H(22)	4939	−1111	2852	461(46)
H(23)	3496	−2342	3050	461(46)
H(25)	1694	−2182	4874	461(46)
H(26)	1395	−739	6413	461(46)
H(171)	3487(61)	5882(41)	5760(96)	1200
H(172)	3130	5572	3522	1200
H(173)	2295	5420	5410	1200
H(271)	1404(61)	−2828(40)	3918(105)	1200
H(272)	1975(62)	−2766(39)	5801(92)	1200
H(273)	600	−2050	5100	1200

Bond lengths and angles are listed in Table 4. The mean C–C length in the phenyl groups (1·387 and 1·385 Å) is slightly less than the standard value (1·394 Å).[12] The bond lengths between the nitrogen and carbon atoms are very similar to the corresponding lengths in two vinylideneamines [7] which have approximately the same angle at the nitrogen atom. The difference between the C(1)–N(1) and C(1)–N(2) lengths appears to be significant (4σ). The N(1)–C(11) and N(2)–C(21) lengths are significantly less than the single-bond value (1·475 Å).[12] The angle at the central carbon atom (170·4°) shows a distortion from the ideal value which is probably due to packing forces and is commonly found in cumulenes.[5-7,13]

TABLE 2

Anisotropic vibrational amplitudes (Å^2 $\times 10^4$) for the non-hydrogen atoms in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	717(17)	899(18)	824(19)	−17(16)	−114(15)	−105(15)
N(2)	656(14)	785(16)	836(17)	38(16)	48(15)	51(14)
C(1)	581(16)	806(19)	757(20)	84(18)	22(15)	−5(15)
C(11)	583(15)	786(17)	589(15)	−15(15)	15(14)	−118(14)
C(12)	575(16)	858(20)	717(19)	−70(17)	−25(15)	−160(15)
C(13)	573(16)	1021(24)	788(22)	−52(21)	19(18)	−59(16)
C(14)	782(20)	873(20)	663(19)	−48(17)	145(17)	6(18)
C(15)	855(23)	854(22)	705(19)	−93(18)	19(19)	−185(19)
C(16)	676(18)	957(23)	679(17)	−16(17)	−53(17)	−151(18)
C(17)	1315(41)	995(30)	1106(38)	−38(28)	63(36)	260(31)
C(21)	600(15)	643(14)	588(14)	28(13)	−29(14)	158(12)
C(22)	696(17)	734(18)	636(16)	4(14)	69(15)	217(15)
C(23)	918(22)	653(16)	657(17)	−35(15)	9(19)	189(17)
C(24)	749(17)	662(15)	551(14)	110(13)	−86(14)	65(15)
C(25)	669(17)	810(18)	591(16)	8(15)	34(14)	58(15)
C(26)	617(15)	687(15)	630(16)	—70(14)	34(14)	103(13)
C(27)	1084(31)	846(24)	895(25)	139(21)	−154(25)	−244(25)

TABLE 3

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

$10F_o/F_o$ (max) *	No.	F_o	F_c	R
0·00—0·10	73	58	52	22·05
0·10—0·13	128	140	125	17·16
0·13—0·16	121	170	155	12·01
0·16—0·20	117	198	186	10·19
0·20—0·24	132	271	255	9·44
0·24—0·28	104	253	248	7·45
0·28—0·34	126	369	365	6·60
0·34—0·40	91	317	312	7·02
0·40—0·50	117	496	501	6·36
0·50—0·64	122	650	654	5·55
0·64—0·90	133	948	964	5·77
0·90—1·55	132	1394	1396	5·57
1·55—10·0	115	2946	2930	4·91
10 sin θ				
0·0—4·0	124	2530	2506	5·21
4·0—5·0	107	1179	1149	6·21
5·0—6·0	153	985	975	6·24
6·0—6·7	147	888	903	5·30
6·7—7·3	141	698	715	6·37
7·3—7·9	166	597	598	5·52
7·9—8·4	163	439	442	7·38
8·4—8·9	162	321	321	8·14
8·9—9·4	184	335	311	10·18
9·4—10·0	164	240	221	12·41
All	1511	8216	8146	6·25

* F_o (max) 94·40.

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

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

[13] G. J. Bullen and K. Wade, *Chem. Comm.*, 1971, 1122.

Table 5 gives equations for some least-squares planes and deviations of atoms from these planes. Planes (1) and (2) show that each nitrogen atom lies close to the plane of the phenyl group to which it is attached. Planes (3) and (4) show that the C=N–C portion of the cumulene chain lies closer to the plane of the phenyl group in **4** than in **3**. This feature is emphasised by the torsion angles quoted in Table 6. The torsion angle C(11)–N(1)–N(2)–C(21) would be 90° for an idealised allene-type structure.

The number and the shortest of the van der Waals contacts are given in Table 7. The packing of the molecules is shown in Figure 2. The crystal structure is layered

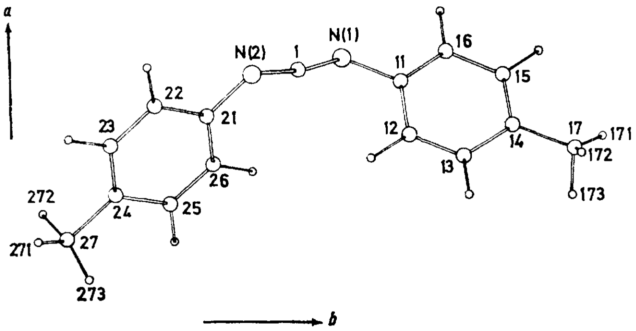

FIGURE 1 Projection down *c* of the asymmetric unit, with the labelling of the atoms

TABLE 4

Bond lengths (Å) and angles (°). Values without estimated standard deviations involve unrefined hydrogen atoms

(*a*) Distances

C(1)–N(1)	1·223(5)	C(14)–C(17)	1·520(6)
C(1)–N(2)	1·204(4)	C(24)–C(27)	1·507(5)
N(1)–C(11)	1·428(4)	C(21)–C(22)	1·389(4)
N(2)–C(21)	1·432(4)	C(22)–C(23)	1·380(5)
		C(23)–C(24)	1·400(5)
C(11)–C(12)	1·397(5)	C(24)–C(25)	1·387(4)
C(12)–C(13)	1·373(5)	C(25)–C(26)	1·373(4)
C(13)–C(14)	1·385(5)	C(26)–C(21)	1·382(4)
C(14)–C(15)	1·390(5)	Mean	1·385
C(15)–C(16)	1·390(5)		
C(16)–C(11)	1·385(4)	C(27)–H(271)	1·001(70)
Mean	1·387	C(27)–H(272)	1·073(67)
		C(27)–H(273)	1·085
C(17)–H(171)	0·965(67)		
C(17)–H(172)	1·090		
C(17)–H(173)	1·086		

(*b*) Angles

N(1)–C(1)–N(2)	170·4(4)	C(13)–C(14)–C(17)	121·4(4)
		C(15)–C(14)–C(17)	121·0(4)
C(1)–N(1)–C(11)	127·2(3)	C(23)–C(24)–C(27)	121·0(3)
C(1)–N(2)–C(21)	128·4(3)	C(25)–C(24)–C(27)	121·1(3)
C(11)–C(12)–C(13)	119·6(3)	C(21)–C(22)–C(23)	120·0(3)
C(12)–C(13)–C(14)	122·1(3)	C(22)–C(23)–C(24)	120·7(3)
C(13)–C(14)–C(15)	117·6(4)	C(23)–C(24)–C(25)	117·8(3)
C(14)–C(15)–C(16)	121·5(3)	C(24)–C(25)–C(26)	122·1(3)
C(15)–C(16)–C(11)	119·5(3)	C(25)–C(26)–C(21)	119·3(3)
C(16)–C(11)–C(12)	119·6(3)	C(26)–C(21)–C(22)	120·1(3)
C(14)–C(17)–H(171)	114·9(40)	C(24)–C(27)–H(271)	117·3(39)
C(14)–C(17)–H(172)	110·3	C(24)–C(27)–H(272)	93·0(34)
C(14)–C(17)–H(173)	107·3	C(24)–C(27)–H(273)	104·8

TABLE 5

Least-squares planes in terms of orthogonal axes coincident with the crystal axes. Deviations (Å) of relevant atoms from the phases are given in square brackets

	Atoms	Equation
Plane (1):	C(11)—(16)	$0{\cdot}4853x + 0{\cdot}0802y - 0{\cdot}8707z = -0{\cdot}9118$

[C(11) 0·007, C(12) −0·005, C(13) −0·003, C(14) 0·008, C(15) −0·005, C(16) −0·002, N(1) −0·022, C(1) 0·291, N(2) 0·697, C(17) 0·052]

	Atoms	Equation
Plane (2):	C(21)—(26)	$-0{\cdot}4898x + 0{\cdot}3688y - 0{\cdot}7900z = -5{\cdot}0772$

[C(21) −0·006, C(22) 0·001, C(23) 0·005, (C24) −0·007, C(25) 0·003, C(26) 0·004, N(1) −0·339, C(1) −0·110, N(2) 0·010, C(27) −0·004]

	Atoms	Equation
Plane (3):	C(11)—(16), N(1), C(1)	$0{\cdot}4908x + 0{\cdot}1197y - 0{\cdot}8630z = -0{\cdot}6382$

[C(11) −0·044, C(12) −0·060, C(13) −0·012, C(14) 0·050, C(15) 0·040, C(16) −0·003, N(1) −0·119, C(1) 0·147]

	Atoms	Equation
Plane (4):	C(21)—(26), N(2), C(1)	$-0{\cdot}4864x + 0{\cdot}3829y - 0{\cdot}7854z = -5{\cdot}0696$

[C(21) 0·013, C(22) 0·001, C(23) −0·012, C(24) −0·023, C(25) 0·006, C(26) 0·025, N(2) 0·046, C(1) −0·056]

TABLE 6

Torsion angles (°) defined as shown

Definition	Angle
C(11)–N(1)–N(2)–C(21)	88·0
C(1)–N(1)–C(11)–C(12)	21·0
C(1)–N(1)–C(11)–C(16)	18·6
C(1)–N(2)–C(21)–C(22)	7·1
C(1)–N(2)–C(21)–C(26)	8·7

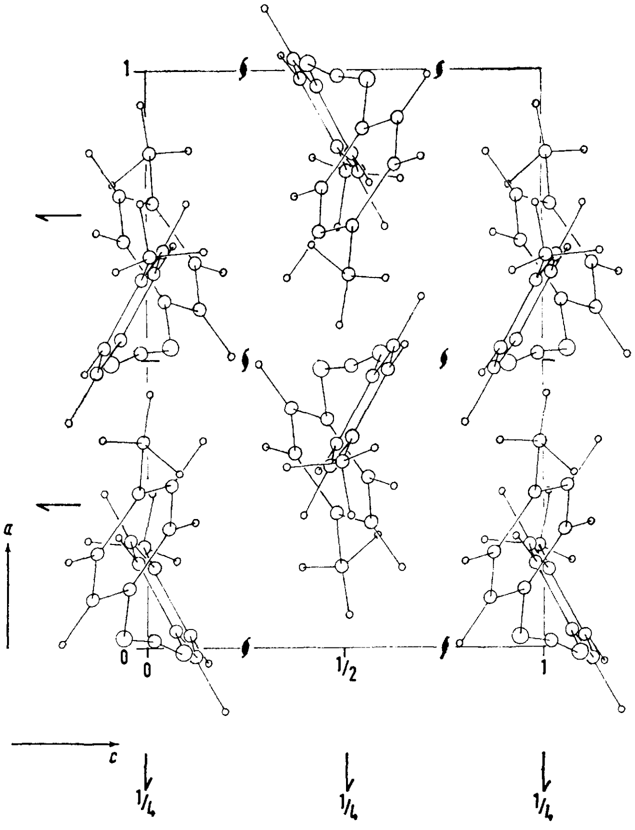

FIGURE 2 Projection of the contents of the unit cell down *b*

in planes parallel to the *ab* plane which intersect the *c* axis at approximately $z = 0$ and $\frac{1}{2}$. The molecule has an approximate two-fold axis.

TABLE 7

Intermolecular contacts (Å)

Contact	No.	Maximum search	Shortest
N · · · C	7	4·0	3·532
N · · · H(Ph)	8	3·7	2·679
N · · · H(Me)	5	3·7	3·110
C · · · C	24	4·0	3·540
C · · · H(Ph)	39	3·7	2·822
C · · · H(Me)	21	3·7	2·783
H(Ph) · · · H(Ph)	7	3·4	2·667
H(Ph) · · · H(Me)	11	3·4	2·634
H(Me) · · · H(Me)	2	3·4	3·023

DISCUSSION

This *X*-ray structure determination shows that di-*p*-tolylcarbodi-imide has approximately the stereochemistry expected on classical grounds. The angles at the nitrogen atoms are close to those expected for trigonal hybridisation. This feature, together with the torsion angle (88°) defined by C(11)–N(1)–N(2)–C(21), gives the molecule an allene-type configuration. The orientation of the phenyl groups relative to the respective C–N=C planes suggests that some conjugation may be taking place between the phenyl groups and the cumulene chain. The C–N lengths are short and nearly the same. There is, however, a significant difference between the C=N lengths (1·223 and 1·204 Å) which can be correlated with the difference in torsion angles (19·8 and 7·9°). The comparison with the vinylidene-amines provides further consistent information about the relationship between the N=C and N–C bond lengths and the value of the angle at the nitrogen atom.[7]

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