393. *The Stereochemistry of Molecules containing the* N=C=N *Group: the Structure of the Monomethiodide of Bis-*p*-dimethylaminophenylcarbodi-imide.*

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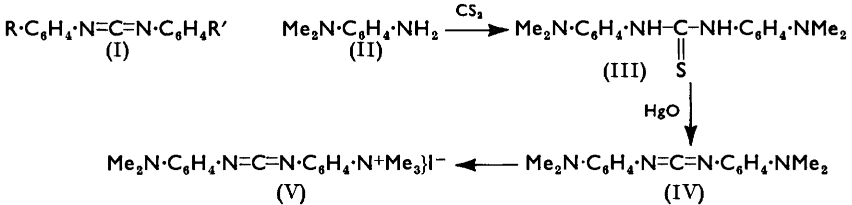
Cell dimensions and space-groups of three carbodi-imides have been determined and the structure of one of them, the monomethiodide of bis-*p*-dimethylaminophenylcarbodi-imide (V) established. This substance is orthorhombic $Pca2_1$ with $a = 40{\cdot}50$ Å, $b = 5{\cdot}67$ Å, $c = 8{\cdot}24$ Å. A two-dimensional analysis based on $hk0$ intensities shows that the shape of the molecule conforms to that predicted by classical stereochemistry. The central C–N=C=N–C chain is bent, in contrast to the linear C=C=N–C chain found in some vinylideneamines. The line containing the N=C=N system does not lie in the plane of either of the benzene rings. This lack of coplanarity is similar to that found in *cis*-azobenzene, and suggests that there is little resonance across the =N– system.

A CARBODI-IMIDE [1] of the type R·N=C=N·R should exist in enantiomorphous forms if the bonds at the nitrogen atoms are not collinear.[2] Attempts have been made to resolve these compounds without success.[3] It has recently been shown [4, 5] that the C=C=N–C chain can be linear, and it therefore seemed possible, notwithstanding reports of a finite dipole moment by Bergmann and Scheutz,[6] that failure to resolve carbodi-imides might be due to the linearity of the C–N=C=N–C chain. However, the *X*-ray examination of a carbodi-imide described below shows that the chain is bent.

EXPERIMENTAL

The carbodi-imides examined were all of the type (I). Samples of di-*p*-tolylcarbodi-imide (I; R = R′ = Me) and bis-*p*-dimethylaminophenylcarbodi-imide (IV) were kindly supplied by Sir Alexander Todd. Further quantities of the latter were made by condensation of *p*-dimethylaminoaniline (II) with carbon disulphide in benzene to give the thiourea (III), followed by removal of hydrogen sulphide with yellow mercuric oxide.[7]



$$\underset{\text{(I)}}{R{\cdot}C_6H_4{\cdot}N{=}C{=}N{\cdot}C_6H_4R'} \qquad \underset{\text{(II)}}{Me_2N{\cdot}C_6H_4{\cdot}NH_2} \xrightarrow{CS_2} \underset{\text{(III)}}{Me_2N{\cdot}C_6H_4{\cdot}NH{-}\underset{\overset{\|}{S}}{C}{-}NH{\cdot}C_6H_4{\cdot}NMe_2} \xrightarrow{HgO}$$

$$\underset{\text{(V)}}{Me_2N{\cdot}C_6H_4{\cdot}N{=}C{=}N{\cdot}C_6H_4{\cdot}N^+Me_3\}I^-} \longleftarrow \underset{\text{(IV)}}{Me_2N{\cdot}C_6H_4{\cdot}N{=}C{=}N{\cdot}C_6H_4{\cdot}NMe_2}$$

(All substituents *para*)

The carbodi-imide (IV) gave the same *X*-ray diagram and had the same melting point as that supplied by Professor Todd. The monomethiodide (V) was prepared by the action of methyl iodide on the base (IV) in benzene [8] and was recrystallised from acetone. The melting point was 165°, as given by Zetzsche and Baum.[8]

The cell dimensions and space-groups of the three carbodi-imides examined are:

R (in I)	R′ (in I)	a (Å)	b (Å)	c (Å)	Space-group	z	$d_{obs.}$ (g./c.c.)	$d_{calc.}$ (g./c.c.)
Me	Me	11·30	14·78	7·70	$P2_12_12_1$	4	—	—
NMe_2	NMe_2	7·46	33·32	6·29	$P2_12_12_1$	4	1·16	1·19
NMe_2	$(NMe_3)^+I^-$	40·50	5·67	8·24	$Pca2_1$	4	1·46	1·48

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[1] Khorana, *Chem. Rev.*, 1953, **2**, 145.

[2] Sidgwick, " The Organic Chemistry of Nitrogen," New edn., revised by Taylor and Baker, Oxford Univ. Press, 1942.

[3] Rolls and Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 2494.

[4] Wheatley, *Acta Cryst.*, 1954, **7**, 68.

[5] Bullough and Wheatley, *ibid.*, 1957, **10**, 233.

[6] Bergmann and Scheutz, *Z. phys. Chem.*, 1932, *B*, **19**, 389.

[7] Zetzsche and Nerger, *Ber.*, 1940, **73**, 467.

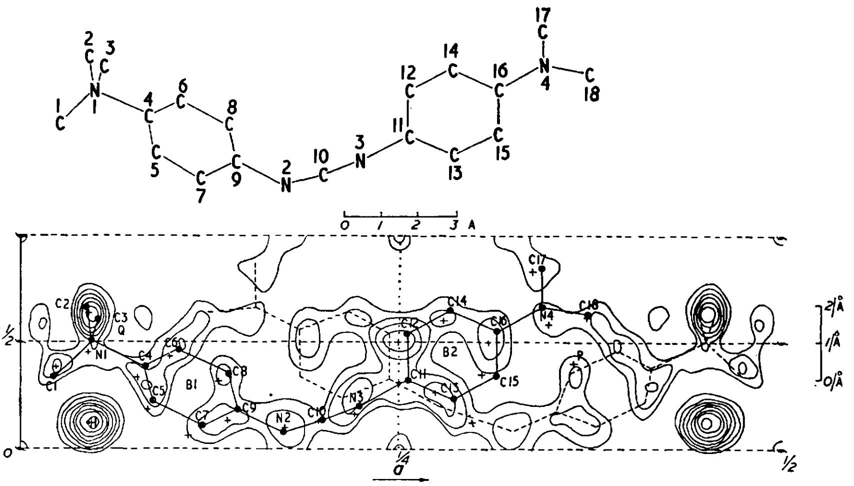
[8] Zetzsche and Baum, *Ber.*, 1942, **75**, 100.

Attempts to find the structure of bis-*p*-dimethylaminophenylcarbodi-imide were unsuccessful and a heavy atom was introduced into this molecule in an attempt to simplify the analysis.

Multiple-film Weissenberg photographs of the *hk*0 and *h*0*l* reflexions from the monomethiodide (V) crystals were taken with Cu-K_α radiation. The intensities were estimated visually by means of a calibration strip. The systematic absences (0*kl*) with *l* odd and (*h*0*l*) with *h* odd give the possible space-groups $Pca2_1$ or *Pcam*. If *Pcam* were correct the molecules would lie on special positions, and, since the monomethiodide cannot possess a centre of symmetry or a twofold axis, the only possibility is that it has a mirror plane. The unit-cell dimensions suggest that this is unlikely. The space-group was confirmed to be No. 29 $Pca2_1$ (C^5_{2v}) by plots of the intensity distribution of the (*h*0*l*) and (*hk*0) projections.[9] (*hk*0) was found to have a centric and (*h*0*l*) a non-centric distribution. The calculated linear absorption coefficient is 145 cm.$^{-1}$. Since the maximum path length of the *X*-rays through the plate-like crystal in the two projections was $1·75 \times 10^{-3}$ cm., absorption errors did not exceed 20% of the observed intensities and were ignored.

The intensities were put on an approximately absolute scale by means of a Wilson plot [10] which gave a value of $B = 3·8$ Å. This value of the temperature factor was retained throughout the analysis.

Electron density $\rho(xy0)$ *contours at arbitrary intervals. Zero contour is at* 3·5 *e per* Å². *The contours for the iodine atom are at ten times the interval of those of the other atoms.*



The X-*Ray Analysis*.—Initial values of the parameters of the iodine atom ($x/a = 0·047$ $y/b = 0·119$, $z/c = 0·250$) were found from the Patterson functions P(*XY*0) and P(*X*0*Z*). Structure factors were then calculated for the iodine atom alone and were found to give a preliminary *R* value of 0·25 and 0·26 for (*hk*0) and (*h*0*l*) respectively. *R*, the so-called "agreement index," is the residual

$$\sum | |F_o| - |F_c| | / \sum |F_o|$$

The signs given by the iodine atom were then used to calculate a Fourier synthesis for the centrosymmetric (*hk*0) projection, all but one of the 75 observed planes being included. As a model with a linear central C–N=C=N–C chain could not be fitted to this Fourier map, atomic positions based on a molecule with the classical configuration

were used to calculate another set of structure factors. The residual immediately fell to 0·19. The Figure shows the second Fourier map which is based on all 75 structure factors. The positions of the atoms assumed at this stage are shown by crosses.

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[9] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

[10] Wilson, *Nature*, 1942, **150**, 152.

All the signs of the structure factors were now known and Fourier difference maps were used for further refinement. The first of these indicated that a methyl group assumed to be at *P* was in the wrong position and should be moved to *Q* (*C*3), thus transferring the quarternary nitrogen atom to the other end of the molecule, closer to the iodide ion. After a few more cycles it became evident that four reflexions (800; 10,00; 12,00; and 510) were affected by extinction. These four reflexions have similar values of sin θ (about 0·17) and there are no planes of lower sin θ with such large intensities. These planes were omitted from subsequent refinement cycles, during which the *R* factor fell to 0·09. The final atomic positions are shown by circles in the Figure. The symmetry-related molecule is shown by broken lines. Table 1 gives the final atomic parameters and Table 2 the observed and calculated structure factors. Since the projection shows that the molecule is bent it was decided not to proceed further with the analysis.

TABLE 1. *Final* x *and* y *parameters.*

	x/a	*y/b*		*x/a*	*y/b*		*x/a*	*y/b*		*x/a*	*y/b*
I	0·0465	0·116	C6	0·106	0·462	C12	0·256	0·539	C18	0·374	0·630
C1	0·024	0·326	C7	0·121	0·103	C13	0·285	0·233	N1	0·048	0·500
C2	0·044	0·660	C8	0·137	0·354	C14	0·283	0·650	N2	0·174	0·072
C3	0·052	0·600	C9	0·144	0·187	C15	0·314	0·340	N3	0·224	0·200
C4	0·083	0·387	C10	0·200	0·132	C16	0·314	0·553	N4	0·343	0·667
C5	0·088	0·233	C11	0·256	0·329	C17	0·343	0·852			

TABLE 2. *Observed and calculated structure factors.* (*Figures are absolute values.*)

h	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c
2	0	—	76·0 + *	0	1	27·6	29·2 +	0	2	37·6	48·0 −
4	0	36·4	51·2 +	1	1	97·6	110·8 +	1	2	88·8	94·4 +
6	0	28·0	33·6 −	2	1	82·0	86·5 +	2	2	0·0	38·8 +
† 8	0	(104·0	144·0) −	3	1	68·8	64·0 +	3	2	112·0	107·2 +
† 10	0	(172·9	220·4) −	4	1	27·2	26·0 +	5	2	139·6	143·2 +
† 12	0	(150·4	183·2) −	† 5	1	(115·6	140·0) +	7	2	144·8	146·4 +
14	0	102·4	106·4 −	6	1	36·8	24·4 +	9	2	76·4	68·0 +
18	0	75·6	72·4 +	7	1	55·2	65·6 +	13	2	109·2	113·2 −
20	0	111·6	117·6 +	8	1	89·2	86·0 −	14	2	48·0	52·8 −
22	0	126·0	130·0 +	9	1	38·4	28·0 +	15	2	133·6	125·2 −
24	0	87·2	90·4 +	10	1	90·0	84·8 −	16	2	51·2	37·6 +
28	0	37·6	33·7 −	11	1	26·4	26·4 +	17	2	120·8	131·2 +
30	0	92·4	95·2 −	12	1	86·4	90·8 −	19	2	55·6	52·4 −
32	0	64·8	59·6 −	13	1	36·8	41·6 −	20	2	29·6	21·6 +
34	0	60·0	59·2 −	14	1	35·6	34·4 −	23	2	43·2	35·6 +
				15	1	49·6	62·8 −	25	2	86·0	81·6 +
0	3	78·0	62·0 −	17	1	46·0	46·4 −	27	2	79·6	83·2 +
2	3	56·0	47·2 −	18	1	66·0	59·2 +	29	2	62·0	56·8 +
3	3	87·2	84·4 +	19	1	58·0	57·2 −				
5	3	67·6	66·8 +	20	1	46·0	52·0 +	0	4	108·8	102·4 −
7	3	85·6	79·2 +	21	1	35·6	36·8 −	2	4	68·4	60·8 +
8	3	53·6	46·0 +	22	1	63·6	62·8 +	8	4	58·8	50·4 +
9	3	26·0	32·0 +	23	1	39·2	41·6 +	10	4	68·8	74·8 +
10	3	55·2	49·2 +	24	1	57·6	54·4 +	12	4	66·8	70·8 +
12	3	56·0	58·0 +	25	1	53·2	50·8 +				
13	3	38·4	34·8 −								
14	3	30·4	28·0 +								
15	3	77·6	79·2 −								
17	3	61·6	61·1 −								
18	3	26·8	36·0 −								
19	3	33·2	39·2 −								
20	3	47·2	55·2 −								

* sin *θ* too low for observation. † Extinguished planes.

DISCUSSION

The following conclusions about the geometry of the molecule can be drawn from the Figure:

(i) The two bonds to N2 are not collinear.

(ii) Those to N3 are approximately collinear in projection, but the shortness of the projected length of N2=C10=N3 (approximately 2·1 Å) shows that these two bonds are considerably inclined to the plane of projection. On the other hand, the approximate regularity of the benzene ring B2 and the normal lengths of the N3–C11 and N4–C16 bonds (1·4 Å) show that these are all approximately parallel to the plane of projection. Thus the C10–N3–C11 system cannot be linear and moreover it does not lie in the plane of the C9–N2–C10 system.

(iii) The plane of the benzene ring B2 is nearly perpendicular to the plane of C10–N3–C11. The angle between B1 and C9–N2–C10 cannot be estimated very accurately but it is easy to see that it is large.

These results show that the molecule has the asymmetric form predicted by classical stereochemistry. Equal numbers of right- and left-handed forms of the molecule occur in the crystal.

The non-coplanarity of the $-C_6H_4-N=C=$ systems resembles that which occurs in *cis*-azobenzene[11] and suggests that there is no conjugation between the central double-bond system and the benzene rings. A carbodi-imide therefore cannot help to discriminate between the two possible effects (electronegativity and hyperconjugation) which, according to Bullough and Wheatley,[5] might account for the linearity of vinylideneamines.

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[11] Hampson and Robertson, *J.*, 1941, 409.