The Crystal and Molecular Structure of α,α'-Dithiobisformamidinium Dichloride

By A. Chiesi Villa, A. Gaetani Manfredotti, M. Nardelli and M. E. Vidoni Tani

Istituto di Chimica Generale ed Inorganica, Università degli Studi, Parma, Italy. Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.

The crystal structure of α,α'-dithiobisformamidinium dichloride, $[SC(NH_2)_2]_2Cl_2$, has been determined and refined by Fourier and least-squares methods using three-dimensional X-ray data collected with a single-crystal diffractometer (Cu $K\alpha$). The unit cell parameters are: $a = 8\cdot78(1)$, $b = 10\cdot52(1)$, $c = 19\cdot69(1)$ Å, $Z = 8$. Space group: *Pbca*. All the hydrogen atoms have been located directly. The dithiobisformamidinium cation is in a general position and is formed by two planar thiourea groups which are slightly rotated with respect to the S–S bond [2·017(2) Å]: $(SCNN)\wedge(SSC) = 6\cdot9°$ and $15\cdot6°$. The internal rotation angle around the S–S bond is $92\cdot3°$. Bond distances and angles in the thiourea groups are in agreement with those found in thiourea and its derivatives. A comparison is made of the corresponding dithiobisformamidinium dibromide and diiodide. Packing is determined by a system of hydrogen bonds of the type $N–H\cdots Cl$ [3·132(5), 3·181(6), 3·120(5), 3·142(6), 3·145(6), 3·150(6) Å].

Introduction

X-ray crystal analysis of dithiobisformamidinium dichloride has been carried out with the aim of defining the molecular conformation of the cation in connexion with that found for the same ion in dithiobisformamidinium dibromide and diiodide monohydrates (Foss, Johnsen & Tvedten, 1958) and in the analogous α,α'-diselenobisformamidinium dichloride (Chiesi Villa, Nardelli & Vidoni Tani, 1970). Another aspect of this research is connected with the study of the structural situation and the effect of the water of crystallization, which is found in the bromide and iodide derivatives, but not in the chloride derivative.

Experimental

α,α'-Dithiobisformamidinium dichloride was prepared by treatment of thiourea with hydrogen chloride in the presence of hydrogen peroxide in an ethanol solution, as described by Presler & Berger (1947). The compound crystallizes in colourless birefringent orthorhombic prisms elongated along [010]. Preliminary crystal data determined from rotation and Weissenberg photographs and refined on a single-crystal Siemens automated diffractometer (Cu $K\alpha$, $\lambda = 1\cdot5418$ Å) are in agreement with those found by Foss, Johnsen & Tvedten (1958): $[SC(NH_2)_2]_2Cl_2$, M.W. 223·1; $a = 8\cdot78$ (1), $b = 10\cdot52$ (1), $c = 19\cdot69$ (1) Å; $V = 1819$ Å³, $Z = 8$, $D_x = 1\cdot63$ g.cm⁻³; $\mu = 100\cdot2$ cm⁻¹ (Cu $K\alpha$), $F(000) = 912$; space group: *Pbca* (from systematic absences).
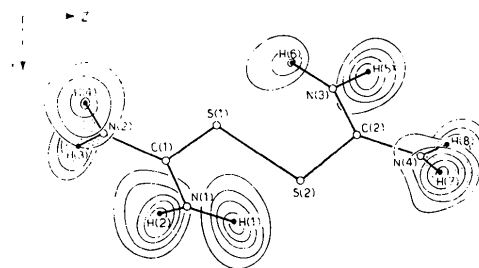

Fig. 1. Composite map of the hydrogen atom distribution from the final $F_o - F_c$ synthesis. Contours are drawn at intervals of 0·1 e.Å⁻³ starting at 0·6 e.Å⁻³.

Table 1. *Final atomic fractional coordinates and temperature factors* $(8\pi^2$ Å²$)$

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are given in the form:

$$\exp[-0\cdot25(h^2 B_{11}a^{*2} + \ldots 2kl B_{23}b^*c^*)]$$

Non-hydrogen atoms: positional parameters × 10⁴

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	4363 (2)	−3197 (2)	−767 (1)	4·63 (7)	4·17 (8)	2·73 (5)	0·11 (6)	1·09 (5)	−0·88 (5)
Cl(2)	397 (2)	−2780 (2)	3226 (1)	5·84 (9)	3·88 (8)	3·36 (6)	0·58 (6)	2·04 (6)	0·19 (6)
S(1)	2322 (2)	635 (1)	783 (1)	4·37 (7)	2·78 (7)	2·02 (5)	0·56 (5)	−0·26 (5)	−0·20 (4)
S(2)	3608 (2)	610 (2)	1632 (1)	3·63 (6)	3·06 (7)	2·12 (5)	−0·60 (5)	−0·15 (5)	−0·02 (4)
N(1)	4136 (6)	−1363 (5)	482 (2)	4·88 (25)	3·25 (23)	2·77 (18)	0·79 (19)	0·01 (17)	−0·34 (18)
N(2)	2518 (7)	−658 (5)	−346 (2)	5·18 (25)	4·77 (30)	1·93 (16)	0·55 (22)	−0·42 (18)	−0·26 (18)
N(3)	1559 (6)	−1207 (5)	1972 (2)	3·79 (22)	3·29 (24)	2·54 (17)	−0·58 (17)	−0·56 (16)	0·01 (17)
N(4)	3054 (6)	−365 (5)	2819 (2)	4·44 (23)	4·00 (27)	2·07 (17)	−0·24 (20)	−0·65 (16)	−0·03 (17)
C(1)	3099 (7)	−590 (6)	270 (3)	3·32 (22)	4·11 (32)	1·97 (19)	−0·17 (21)	0·22 (17)	−0·03 (19)
C(2)	2593 (7)	−424 (6)	2183 (3)	3·01 (21)	3·57 (28)	2·12 (18)	0·24 (19)	−0·08 (18)	−0·15 (18)

Table 1 (cont.)

Hydrogen atoms: positional parameters × 10³

	x/a	y/b	z/c	B
H(1)	432 (7)	− 202 (5)	20 (3)	2·9 (1·3)
H(2)	449 (8)	− 128 (7)	94 (3)	4·8 (1·5)
H(3)	277 (8)	− 141 (7)	− 60 (4)	5·1 (1·7)
H(4)	181 (10)	− 17 (7)	− 52 (4)	7·7 (1·9)
H(5)	116 (7)	− 178 (5)	233 (3)	3·8 (1·4)
H(6)	96 (9)	− 114 (8)	155 (4)	8·4 (1·9)
H(7)	345 (9)	37 (7)	303 (4)	7·1 (1·8)
H(8)	279 (7)	− 108 (7)	309 (3)	4·4 (1·5)

Three-dimensional intensity data were collected by an 'on line' single-crystal automated Siemens diffractometer using the $\omega/2\theta$ scan technique (2θmax = 140°) with the crystal aligned with its elongation coinciding with the axis of the diffractometer (Ni-filtered, Cu $K\alpha$ radiation). In this way 1626 independent reflexions were measured, of a possible 1641; excluding the reflexions with $I \leq 2\sigma(I)$, there remained 1211 intensity readings which were used in the successive analysis and refinement. The sample used to collect data was roughly a cylinder with a mean cross radius of 0·5 mm; no absorption correction was made so the thermal coefficients given in Table 1 are influenced by this omission.

The structure amplitudes were found after the usual Lorentz–polarization reduction and put on an absolute scale by successive comparison with the calculated values.

Determination of the structure and refinement

The structure was solved by the heavy-atom method starting from the coordinates of the sulphur atoms deduced from a three-dimensional Patterson calcu-

lation. The refinement was begun when all the coordinates were found (excepting the hydrogen atoms), the conventional R being 19·6 %. Block-diagonal least-squares with anisotropic thermal parameters were used. The function $\sum w|\Delta F|^2$ was minimized using the weighting coefficients derived from the $\langle|\Delta F|\rangle$ vs. $|F|$

(a)

(b)

(c)

Fig. 3. Projections of the structures: (a) [SC(NH₂)₂]₂Cl₂ on (010); (b) [SC(NH₂)₂]₂Br₂.H₂O along [010]; (c) [SC(NH₂)₂]₂I₂.H₂O on (001).
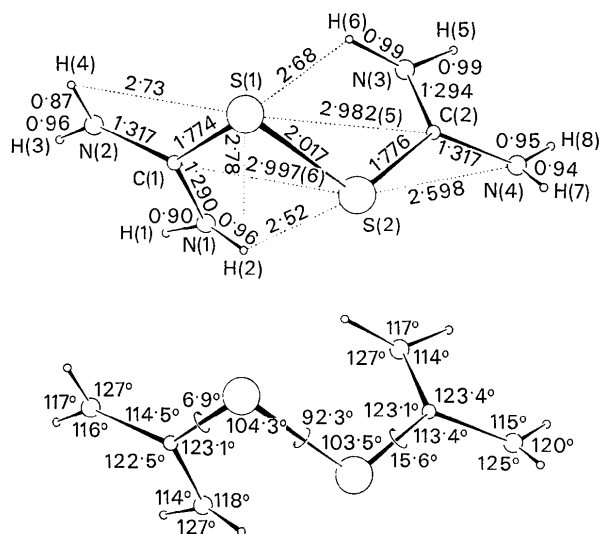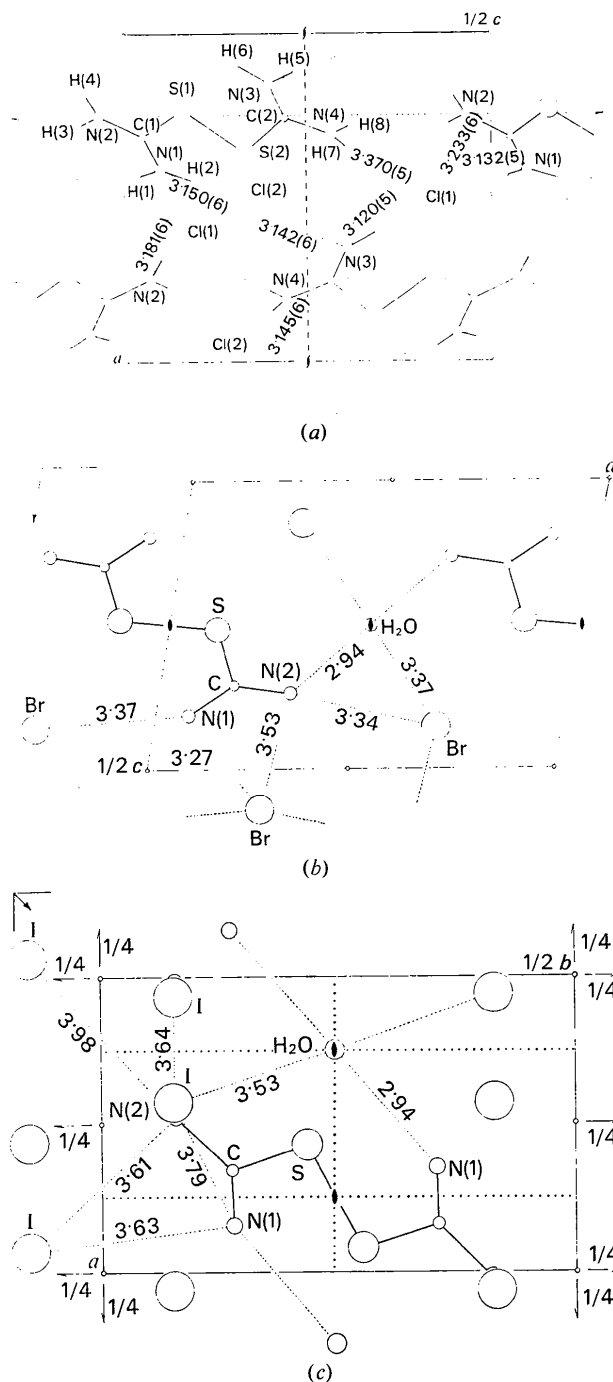

Fig. 2. Distances and angles in the organic cation. The standard deviations (not quoted in Figure) for the distances and angles involving the hydrogen atoms are in the range 0·06–0·08 Å and 3–7° respectively.

Table 2. Comparison of the structural parameters of the cation $^+(NH_2)_2CXXC(NH_2)_2^+$ $(X=Se,S)$
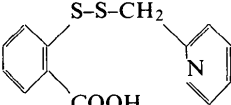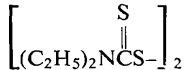
Interatomic distances	Cl(NH₂)₂CSSC(NH₂)₂Cl* 2·017 (2) Å		Br(NH₂)₂CSSC(NH₂)₂Br† 2·044 (10) Å	I(NH₂)₂CSSC(NH₂)₂I† 2·044 (20) Å	Cl(NH₂)₂CSeSeC(NH₂)₂Cl‡ 2·380 (6) Å
S(1)–S(2)		X–X¹			
S(1)–C(1)	1·774 (6)	X–C	1·78 (3)	1·75 (4)	1·94 (1)
S(2)–C(2)	1·776 (6)				
C(1)–N(1)	1·290 (8)	C–N	⎰ 1·33 (3)	⎰ 1·33 (4)	⎰ 1·32 (2)
C(1)–N(2)	1·317 (7)		⎱ 1·33 (3)	⎱ 1·36 (4)	⎱ 1·30 (2)
C(2)–N(3)	1·294 (8)				
C(2)–N(4)	1·317 (7)				
Bond angles					
S(2)S(1)C(1)	104·3 (2)°	X¹XC	104·0°	98·9°	95·5°
S(1)S(2)C(2)	103·5 (2)				
S(1)C(1)N(1)	123·1 (4)	XCN	⎰ 121·2	⎰ 122·9	⎰ 117·7
S(1)C(1)N(2)	114·5 (5)		⎱ 118·3	⎱ 113·1	⎱ 119·6
S(2)C(2)N(3)	123·1 (4)				
S(2)C(2)N(4)	113·4 (4)				
N(1)C(1)N(2)	122·5 (6)	NCN	119·0	116·3	122·7
N(3)C(2)N(4)	123·4 (5)				
Interplanar angles					
∠[S(1)S(2)C(1)]/[S(1)S(2)C(2)]	92·3°	∠(X¹XC)/(XX¹C¹)	89·2°	104·8°	89·5°
∠[S(1)C(1)N(1)N(2)]/[S(2)S(1)C(1)]	6·9	∠(XCNN)/(X¹XC)	1·6	14·5	90·6
∠[S(2)C(2)N(3)N(4)]/[S(2)S(1)C(2)]	15·6				

* Present paper.
† Foss, Johnsen & Tvedten (1958).
‡ Chiesi Villa, Nardelli & Vidoni Tani (1970).

Table 3. *Comparison of parameters in compounds containing a -CSSC- grouping*

	S-S	C-S-S angle	Dihedral angle -CSSC-	C-S	Reference
(structure: S-S-CH2 ... COOH)	2·04 Å	{ 103·6° 105·1	99·1°	{ 1·83 Å 1·80	Karle, Karle & Mitchell (1969)
[(C2H5)2NCS-]2 (with S=)	2·00	{ 103·4 103·6	96·4	{ 1·82 1·81	Karle, Estlin & Britts (1967)
(CH3)2NCSSC(CH3)3	2·00	{ 106·1 105·4	99·6	{ 1·80 1·85	Mitchell (1969)
L-Cystine.HCl	2·04	103·0	101	1·87	Steinrauf, Peterson & Jensen (1958)
N,N'-Diglycyl-L-cystine.2H2O	2·04	103·8	101	1·86	Yakel & Hughes (1954)
HgI2[S2CN(CH3)2]2	2·03	{ 105·1 106·9	89·2	{ 1·79 1·84	Beurskens, Cras, Noordik & Spruijt(1971)
(C6H5.CH2)2S2	2·03	{ 105·8 106·5	96·2	{ 1·79 1·81	Lee & Bryant (1969)
2,2'-Diaminodiphenyl disulphide	2·06	{ 103·2 103·5	90·5	{ 1·77 1·75	Lee & Bryant (1970)
Bis-(o-nitrophenyl) disulphide	2·045	{ 104·6 104·3	85·1	{ 1·784 1·808	Ricci & Bernal (1970)

distribution as described by Stout & Jensen (1968). At this point the conventional R value was 8·3%. All the hydrogen atoms were located from the final $\varrho_o-\varrho_c$ map (Fig. 1) and the complete least-squares refinement improved the conventional R index to 7·5%.

Table 1 shows the final atomic parameters and the corresponding e.s.d.'s. Observed and calculated structure factors are stored at the National Lending Library and copies are available from the authors on request.

The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for Cl, S, N and C and those of Stewart, Davidson & Simpson (1965) for H.

All the calculations were performed on the C.D.C. 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), using programs of Immirzi (1967).

Description of the structure and discussion

The dithiobisformamidinium cation is in a general position, so the two thiourea parts in it are crystallographically independent. Bond distances and angles are given in Table 2 and in Fig. 2. The S-S distance is a little shorter than two covalent single bond radii (1·04 Å, Pauling, 1960) and is in agreement with those found for the same ions in the bromide and iodide salts as shown in the data of Table 2, in which the structural parameters of the cation in the three halides and in the analogous selenium derivative are compared. The sulphur-sulphur distance also agrees with those found in other open chain disulphides as shown in Table 3, which gives the structural parameters of the -CSSC- group of a few compounds. The bond angles on the sulphur atoms [104·3 (2)° and 103·5 (2)°] agree with the data quoted in Tables 2 and 3. The S-S bridge conformation is similar to that observed in the compounds quoted in those tables; the internal rotation

angle around the S-S bond is 92·3°. The S(1)-C(1) and S(2)-C(2) distances [1·774 (6) and 1·776 (6) Å] are equal and correspond to single bonds, while the C-N distances [1·290 (8), 1·317 (7), 1·294 (8), 1·317 (7) Å], which do not differ significantly from one another, show a remarkable π delocalization along the N-C-N systems.

The two thiourea parts of the cation are both planar; their least-squares planes are: S(1)C(1)N(1)N(2): $0·7054x+0·6278y-0·3289z=1·3507$; S(2)C(2)N(3) N(4): $0·6867x-0·7080y-0·1641z=1·1932$. The dihedral angle they form is 95·4°, so their orientation is of the same type as that found in the corresponding bromide (91·9°) and iodide (90·1°). The internal rotation angles around S(1)-C(1) and S(2)-C(2) are 6·9° and 15·6° respectively. The first value agrees with that found in the bromide (1·6°) and the second one with that found in the iodide (14·5°). As shown in Table 2, the

Table 4. *Intermolecular contacts*

i	½-x	y-½	z
ii	½+x	-½-y	z̄
iii	x-½	y	½-z
iv	½-x	½+y	z
v	x̄	½+y	½-z
vi	x	-½-y	z-½

Hydrogen bonds

Cl(1)···N(1)	3·132 (5) Å	Cl(1)-H(1) —N(1)	159 (7)°
Cl(1)···N(2)	3·233 (6)	Cl(1)-H(3) —N(2)	127 (7)
Cl(1)···N(2i)	3·181 (6)	Cl(1)-H(4i)--N(2i)	155 (7)
Cl(1)···N(3ii)	3·120 (5)	Cl(1)-H(6ii) -N(3ii)	155 (7)
Cl(2)···N(3)	3·142 (6)	Cl(2)-H(5) —N(3)	140 (7)
Cl(2)···N(4i)	3·145 (6)	Cl(2)-H(7i)--N(4i)	164 (7)
Cl(2)···N(1iii)	3·150 (6)	Cl(2)-H(2iii)-N(1iii)	122 (7)

Other contacts less than 3·5 Å

S(1) ···N(1iv)	3·460 (6) Å
S(2) ···N(3iv)	3·419 (6)
S(1) ···Cl(2v)	3·505 (3)
Cl(1)···N(4vi)	3·370 (5)
N(3)···N(4iii)	3·229 (8)

corresponding value in the selenium derivative is much larger (90·6°). This means that the different orientation of the $-XC(NH_2)_2$ groups in the seleno- and thio-derivatives is not only due to packing requirements, but is related to the different size of selenium with respect to sulphur and to the possibility of orbital interactions concerning the $X-X$ and $X-C$ bonds.

The positions of the chlorine atoms are mainly determined by their interactions with the NH_2 groups; these interactions hold the whole structure together. The contacts which could be considered as hydrogen bonds and other intermolecular contacts less than 3·5 Å are listed in Table 4.

It is interesting to compare the present structure with those of the bromide and iodide derivatives which are shown in the projections in Fig. 3. The differences in these three structures are mainly due to the fact that hydrogen bonding between the NH_2 group and the halide ion decreases with the increase of the halogen radius: so the $N-H\cdots O$ interactions are prefered with respect to the $N-H\cdots I^-$ (or Br^-). Consequently the bromide and iodide derivatives crystallize as hydrates, while the chlorine derivative is anhydrous.

References

BEURSKENS, P. T., CRAS, J. A., NOORDIK, J. H. & SPRUIJT, A. M. (1971). *J. Cryst. Mol. Struct.* 1, 93.

CHIESI VILLA, A., NARDELLI, M. & VIDONI TANI, M. E. (1970). *Acta Cryst.* B26, 1504.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321.

FOSS, O., JOHNSEN, J. & TVEDTEN, O. (1958). *Acta Chem. Scand.* 12, 1782.

IMMIRZI, A. (1967). *Ric. Sci.* 37, 743.

KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* 22, 273.

KARLE, J., KARLE, I. L. & MITCHELL, D. J. (1969). *Acta Cryst.* B25, 866.

LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* B25, 2094.

LEE, J. D. & BRYANT, M. W. R. (1970). *Acta Cryst.* B25, 2497.

MITCHELL, D. J. (1969). *Acta Cryst.* B25, 998.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Ithaca: Cornell Univ. Press.

PRESLER, P. W. & BERGER, L. (1947). *J. Amer. Chem. Soc.* 69, 322.

RICCI, J. S. & BERNAL, I. (1970). *J. Chem. Soc. (B)*, p. 806.

STEINRAUF, L. K., PETERSON, J. & JENSEN, L. H. (1958). *J. Amer. Chem. Soc.* 80, 3835.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 455. New York: Macmillan.

YAKEL, H. L. & HUGHES, E. W. (1954). *Acta Cryst.* 7, 291.

The Crystal and Molecular Structure of a Methylated Photoproduct of Thymine–Uracil, Containing Four Pyrimidine Nuclei

BY J. L. FLIPPEN, R. D. GILARDI AND I. L. KARLE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., 20390, U.S.A.

The structure of a pyrimidine tetramer, $C_{24}H_{28}N_8O_6$, was determined through single-crystal X-ray diffraction analysis using diffractometer data. This molecule was produced by irradiating an aqueous solution of a thymine–uracil adduct, 6,4'-(pyrimidin-2'-one)-thymine, with relatively long-wavelength ultraviolet(UV) irradiation (310–360 nm). The adduct is itself a photoproduct isolated in minute quantities from UV-irradiated deoxyribonucleic acid (DNA). The compound crystallizes in the monoclinic space group $P2_1/c$ with three molecules of H_2O per asymmetric unit. Cell dimensions are: $a = 7·117 \pm 0·003$, $b = 21·348 \pm 0·016$, $c = 18·237 \pm 0·006$ Å and $\beta = 98·6 \pm 0·2°$. The tetramer contains a 12-membered ring comprising carbon atoms from each pyrimidine ring, plus two methylene groups. The structure was solved directly by the symbolic-addition procedure.

Introduction

Several photoproducts derived from pyrimidine bases have now been isolated from UV-irradiated DNA both *in vivo* and *in vitro* (Wang & Varghese, 1967; Varghese & Wang, 1967). The formation of these products, and also subsequent transformations of these products by

UV light, are being studied to provide a basis for understanding radiation damage in living organisms.

The simplest and most abundant photoproducts from pyrimidines are the cyclobutyl-type dimers. Many of these dimers have been characterized and their crystal structures have been reported (*e.g.* Gibson & Karle, 1971; Konnert & Karle, 1971; Camerman, Weinblum