

Table 4. Contingency table of  $(x_i - x_o)^2$ , and results of  $\chi^2$  test for the hypothesis that the mean-square lengthening of C(1)-C(7) is equal to the mean-square shortening

Intervals	0 ↓ $1 \times 10^{-4}$	$1 \times 10^{-4}$ ↓ $2 \times 10^{-4}$	$2 \times 10^{-4}$ ↓ $3 \times 10^{-4}$	$3 \times 10^{-4}$ ↓ $4 \times 10^{-4}$	$4 \times 10^{-4}$ ↓ $10 \times 10^{-4}$	$10 \times 10^{-4}$ ↓ $16 \times 10^{-4}$	$16 \times 10^{-4}$ ↓ $\infty$
Number of distances in sample	43	17	9	13	4	7	10
Number of distances if $\chi^2$ distribution	33.7	15.3	7.1	6.1	22.4	10.2	7.1

$\chi^2 = 30.5$  and  $\chi^2(4, 0.95) = 9.5$ ; thus the hypothesis can be rejected.

Table 5. Comparison of the geometry of averaged X-ray fragments with the geometry of unsubstituted norbornane

	X-ray	Electron diffraction	Ab initio
<b>Bond lengths (Å)</b>			
C(1)-C(2)	1.544	1.536	1.545
C(1)-C(7)	1.535	1.544	1.544
C(2)-C(3)	1.559	1.573	1.576
(CC)	1.546	1.547	1.553
<b>Valence angles (°)</b>			
C(1)-C(2)-C(3)	103.0	102.7	103.1
C(2)-C(1)-C(6)	108.2	109.0	108.0
C(2)-C(1)-C(7)	101.8	102.0	101.6
C(1)-C(7)-C(4)	94.3	93.4	94.6
<b>Torsion angles (°)</b>			
C(6)-C(1)-C(2)-C(3)	71.2	-71.6	-71.3
C(2)-C(1)-C(7)-C(4)	55.5	-56.3	-55.7
C(7)-C(1)-C(2)-C(3)	35.1	35.8	35.1
C(1)-C(2)-C(3)-C(4)	4.8	0.0	0.0

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## A Revision of van der Waals Atomic Radii for Molecular Crystals: N, O, F, S, Cl, Se, Br and I Bonded to Carbon

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### Abstract

The Cambridge Structural Database has been used to determine the effective non-bonding (van der Waals) shapes of N, O, F, S, Cl, Se, Br and I atoms. In all cases these atoms were bonded to a single carbon atom. For O and N, the shapes are virtually spherical but for the remainder, the shape is more or less spheroidal, always having the shorter radius along the atom-to-carbon bond vector ('polar flattening'). The results imply that these effective shapes are

transferable from crystal to crystal only so long as the immediate chemical environment of the non-bonded atom is not changed. Some implications for intermolecular force theory are briefly discussed.

### Introduction

The non-bonding (van der Waals) atomic radii currently widely used for molecular crystals are taken from tables of Pauling (1942), or that, somewhat

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revised, of Bondi (1964, 1968). These tabulations were doubtless prompted by the original hope (i) that the effective shapes of non-bonded atoms are spherical about their nuclei (the possibility of non-spherical shapes has been raised by Bondi), (ii) that such radii are additive and (iii) that the radii are not affected either by the nature of the other atom(s) to which the atom of interest is chemically bonded or by the nature of the chemical bond(s) involved.

The shortest distance  $d_{XY}$  found between non-bonded atoms  $X$  and  $Y$  is a consequence of the intermolecular forces between the molecule containing the atom  $X$  and all the other molecules in the crystal containing the atom  $Y$  (in most crystals the molecules are all chemically identical). It would be surprising if these forces were such as to give the same effective shapes to the atoms  $X$  and  $Y$  whatever their chemical environments.

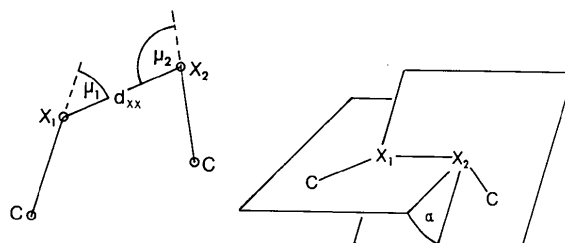
In this paper we show that these shapes are often not spherical, being shorter in their 'head-on' contacts than in their 'sideways-on' contacts. These contact distances are also certainly chemical-environmentally dependent. It is now clear that the earlier tabulations, ascribing spherical effective shapes to non-bonded atoms, were very approximate. For many atoms the assigned radius was close to that now found for sideways contacts. Nevertheless, details concerning the effective shapes of non-bonded atoms in crystals, obtained from large databases, are still needed for deciding whether or not a particular non-bonded distance is abnormally short; they are also needed in order to understand the nature of the intermolecular forces involved.

We have already shown earlier (Nyburg & Szymański, 1968; Nyburg, 1979), from very small data sets, that non-bonded atoms are often not spherical, exhibiting 'polar flattening'. In the present paper we use the Cambridge Structural Database (CSD) (Allen *et al.*, 1979) containing entries for some 35 000 organic crystal structures.\* From this database we have extracted data concerning the shortest non-bonded distances between certain atoms of Groups V, VI and VII. We have confined our attention to subsets of the data in which the two non-bonded atoms are of the same kind and where the immediate chemical environment of the atom in question was the same, *i.e.* bound, by the same kind of chemical bond, to only one other atom (carbon). The results show that although polar flattening is not found for O or N in the chosen chemical environments, and the effect is small in F, the other atoms show pronounced flattening.

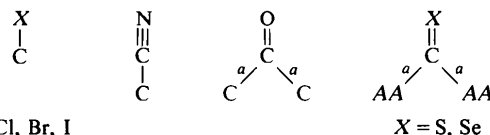
#### Data retrieval

CSD, as currently available, comes with a number of subprograms for retrieving bibliographic, crystal

structure and connectivity data. However, although non-bonded distances up to some given limiting distance can be retrieved for any atom in a crystal structure, it is not possible to retrieve directly the  $\mu$  (polar) or  $\alpha$  (torsion) angles (see below) required in this survey. Thus a number of additional subprograms had to be written to retrieve these data in the form required.



The survey was restricted to distances  $X \cdots X$  where  $X$  is any of the atoms N, O, F, S, Cl, Se, Br and I. In all eight cases these atoms were themselves bonded to only a single carbon atom by either a single (F, Cl, Br, I), double (O, S, Se), or triple (N) bond. The first part of the retrieval consisted in searching for molecules in crystals with the following connectivities:



where  $a$  indicates any type of bond (otherwise the bonds were exactly as written) and AA means any atom. The somewhat different connectivity restrictions made for O on the one hand and for S and Se on the other were made to ensure sufficient data were retrieved. The retrieved reference codes (REFCODES) for crystal structures containing the above connectivities were then searched twice to form two new files: (i) for the presence of  $X \cdots X$  distances up to well in excess of twice the currently accepted van der Waals radii and (ii) the fractional coordinates of the  $X$  atom(s) and carbon atom(s) to which they were bonded. These two files were merged and, from this, a new file generated giving all the orthogonal coordinates of the required atoms over all the symmetry positions. This file also contained the required calculated  $\mu_1$  and  $\mu_2$  angles.

To ensure that hydrogen bonding was not playing a role in governing  $X \cdots X$  distances, the file was checked for any  $X \cdots H$  distances shorter than: N 2.9, O 2.5, S 2.8, Se 3.0 Å (Schuster, Zundel & Sandorfy, 1976).  $X$  atoms thus involved were eliminated. One further purge was required for molecules which contained more than one N, O, S or Se atom. This arose because of a peculiarity in the connectivity routine of the GEOM procedure in CSD. This particular

\* As at 21 December 1982; since updated.

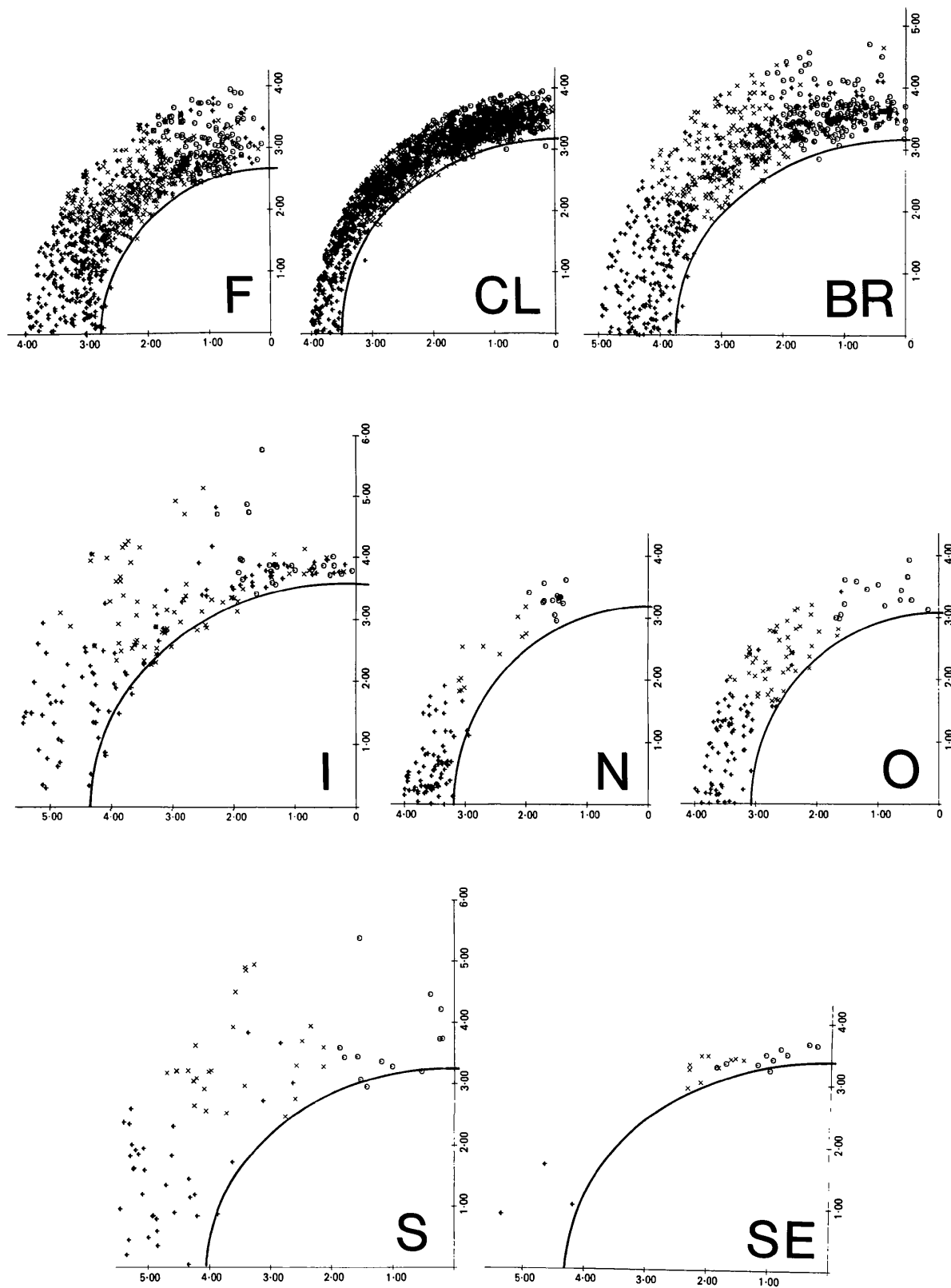


Fig. 1. Polar scatterplots of  $d_{XX}$  (Å) versus  $\mu$  (measured counterclockwise from the vertical). The smaller value of  $\mu$  is that plotted. The larger  $\mu$  value is designated according to its magnitude: 0–30°, circles; 30–60°, crosses; 60–90°, arrows. Note a marked tendency for the two  $\mu$  values to be in the same range. This is commonly due to the fact that  $d_{XX}$  spans a centre of symmetry or diad axis.

connectivity routine is unable to check automatically for the nature of the bonds joining the connected atoms. Thus although in any  $X \cdots X$  distance one  $X$  atom is certainly multiply bonded to a single carbon atom, the other  $X$  atom could be divalent. To overcome this, a bond-length criterion was applied to all C-to- $X$  distances to ensure they corresponded to the required bond multiplicity.

### Results

In order to establish the effective non-bonded shape of atom  $X$  we first obtained scatterplots of  $d_{XX}$  against the mean of  $\mu_1$  and  $\mu_2$  for those cases where  $|\mu_1 - \mu_2| \leq 10^\circ$ . In these plots it was decided to limit  $\mu_1, \mu_2$  arbitrarily to  $90^\circ$ . Beyond this value the effective shape is increasingly influenced by the non-bonded interactions between atoms other than  $X$  in the molecule. The next scatterplots were designed to test whether, for any pairs of values  $\mu_1$  and  $\mu_2$ ,  $d_{XX} = r(\mu_1) + r(\mu_2)$ ,  $r(\mu_i)$  ( $i = 1, 2$ ) having been established from the initial plots. These second plots, Fig. 1, in which the value of  $\mu$  plotted was always the lesser of  $\mu_1, \mu_2$ , matched the initial plots extremely well, implying that the radii  $r(\mu)$  are closely additive for all atoms studied for  $\mu_1, \mu_2$  values up to  $90^\circ$ . In nearly all such scatterplots, it is possible to describe a smooth curve forming a clear boundary between non-bonded distances which are commonly found and non-bonded distances which are rarely, if ever, found. For some atoms there were a few points which had, in this sense, to be regarded as anomalous, that is, having unusually short  $d_{XX}$  values. All such points could be subsequently eliminated for the various reasons given in detail later. For N, and particularly Se, there were fewer data points retrieved than for the other atoms and the boundary curve defining the effective shape could not be drawn with the same degree of confidence.

Apart from N and O it will be seen that the boundaries appear to be those of an ellipse with the minor and major axes at  $\mu = 0, 90^\circ$ . For N and O the boundaries appear circular and for F the ellipticity is small. We can thus represent the boundary curves as  $d_{XX} = 2r_{XX} = 2ab[(a^2 \cos^2 \mu + b^2 \sin^2 \mu)^{-1/2}]^*$  where  $a, b$  are major and minor radii. Values of  $a$  and  $b$  established this way are given, together with the earlier Pauling/Bondi values, in Table 1.

A plot of  $a$  and  $b$  against atomic number (Fig. 2) shows similar trends for Group VI and Group VII elements. The elements of the first period, O and F (and N in Group V), have almost spherical shapes, while for higher members of the group the ellipticity increases. In every case  $a \geq b$ , so that polar flattening is confirmed for all the elements studied here.

\* In terms of 'bond' angle,  $\omega$ , C- $X \cdots X$ , this equation becomes  $d_{XX} = 2ab[(a^2 \sin^2 \omega + b^2 \cos^2 \omega)^{-1/2}]$ .

Table 1. *Effective radii of atoms* (Å)

	(i)*	(ii)†	(iii)‡
F	1.47	1.38	1.30
Cl	1.76	1.78	1.58
Br	1.85	1.84	1.54
I	1.98	2.13	1.76
N	1.70	1.60	1.60
O	1.50	1.54	1.54
S	1.74	2.03	1.60
Se	2.00	2.15	1.70

\* Spherical values given by Bondi (1964, 1968), except for Se (Pauling, 1942).

† Major radius,  $a$ .

‡ Minor radius,  $b$ .

An attempt was made to see whether the dihedral angle,  $\alpha$ , was correlated with the effective shape. Restricting  $\alpha$  to even quite large angular ranges, say  $30^\circ$ , drastically reduced the number of data points left for any one scatterplot. For such plots as could be made we found no effect of  $\alpha$  on the non-bonding shape.

For some of the initial  $d_{XX}$  vs  $\mu$  scatterplots, there were no anomalous points lying within the elliptical boundary curve. For others there were several such points. In each case we referred to the original publication. We were able to eliminate all these points for one or more of the following reasons:

(i) disordered crystal structure in which it was clear that two atoms  $X$  of occupancy  $< 1.0$  could not simultaneously occupy their sites.\* Cl: CLNPHT, MCMANT10, CLYTPYR; N: CBZTCQ;

(ii) exceptionally large temperature factors for one or other of the  $X$  atoms: Cl: CACTFE;

\* See Table 2 for bibliographic details.

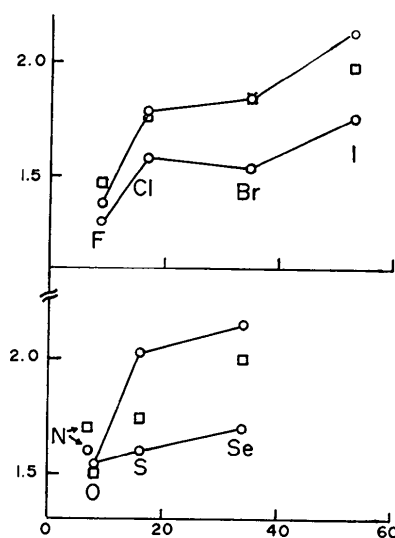


Fig. 2. Circles, major and minor spheroidal atomic radii (Å) from Table 1; squares, Pauling/Bondi spherical radii (Å). Horizontal axis: atomic number.

Table 2. *Bibliographic details*

A full list of references has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42140 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England

REFCODE	Reference	
BARTIX	81 ZNBAD2	36 1187
BARZEZ	81 JACSAT	103 4616
CACTFE	78 JACSAT	100 3375
CBZTCQ	73 BCSJA8	46 2675
CLNPHT	80 CSCMCS	9 699
CLYTPYR	73 JCPKBH	314
CPCPRO	73 CHBEAM	106 935
CPYSUR	80 ASBSDK	36 2170
DHANTQ01	66 ACCRA9	21 927
DIBZPO	70 ASBSDK	26 1999
IPHOAC	Yu, H.-F., Chen, T.-M., Liu, S.-H. & Lin, T.-C. (1980). <i>Ko Hsueh Tung Pao</i> , <b>25</b> , 934-936	
LIACAC	75 ASBSDK	31 1745
MCMANT10	77 JACSAT	99 595
MECPFF	80 KOKHDC	6 1275
MECYBC	75 ICHAA3	14 281
MTDZDT	74 JCPKBH	1096
PYRZON	78 JAFCAU	26 511
TITYRAN	74 ASBSDK	30 1832

- (iii) combination of (i) and (ii): Cl: CPYSUR;  
 (iv) space group wrongly assigned in CSD: O, Cl: BARZEZ;  
 (v) structural data correct but typographical error(s) in published crystal data copied into CSD: Cl: CPCPRO, PYRZON, MTDZDT;  
 (vi) space-group origin used in CSD not that used by authors: I: DIBZPO;  
 (vii) structure appears correct but unaccountable changes made in CSD: I: TITYRAN;  
 (viii) inaccurate structure analysis (two-dimensional photographic data, high R): I: IPHOAC;  
 (ix) distances between X atoms assigned as intermolecular but actually intramolecular: N: MECYBC; O: LIACAC;  
 (x) hydrogen atoms not located by authors but suspected to play a role in X...X distance: O: DHANTQ01, BARTIX, MECPFF.

The revelation of these anomalies and errors proved a valuable byproduct of the survey. Ideally, every crystal structure should have been checked this way, but clearly this is not feasible. In fact, only data points lying within and up to the inner edge of the boundary curves were examined individually. There are probably several other data points in these scatterplots which should be moved or even removed completely.

The exact placing of the ellipses was subjective, being drawn in such a way that only a very small number of data points, if any, remained within the boundary. No error analysis is possible for such a procedure but we estimate the tabulated values of *a* and *b* to be about  $\pm 0.03$  Å for most atoms and somewhat less reliable for N and Se.

Table 3. *Effective radii of atoms (Å), from small data sets*

Source of data	<i>a</i>	<i>b</i>	Reference
F Halogen fluorides	1.55	1.34	Nyburg & Szymański (1968)
Cl Cl <sub>2</sub>	1.90	1.67	Nyburg (1979)
Br Br <sub>2</sub>	2.01	1.64	Nyburg (1979)
I I <sub>2</sub>	2.16	1.76	Nyburg (1979)
N [Ni(CN) <sub>4</sub> ] <sup>2-</sup>	1.65	1.25	Musselman, Stecher & Watkins (1980)
O [Co(CO) <sub>4</sub> ] <sup>-</sup>	≈ 1.74	1.35	Klüfers (1984)

### Results from less extensive surveys

Table 3 sets out the results of a number of surveys of *a* and *b* based on very limited data sets. Note that the derivation of *a* and *b* parameters for Cl, Br and I, based on the crystal structures of the dihalogens, is unusual in that the very few data points which these structures generate are all based on simultaneous contacts of one X atom with several others. In the CSD survey, involving much larger molecules, such multiple contacts seldom occur. Although every example in this table exhibits polar flattening (*a* > *b*), the values obtained differ, often quite markedly, from those found in the present CSD survey. Thus, in the present survey, the value of *b* needed to explain the shortest  $-C\equiv N\cdots N\equiv C-$  contacts is 1.60 Å whereas for  $N\cdots N$  contacts between [Ni(CN)<sub>4</sub>]<sup>2-</sup> ions it is 1.25 Å. This can only mean one of two things: either there are structures containing  $-C\equiv N\cdots N\equiv C-$  contacts consistent with *b* = 1.25 Å but which have not yet been structurally analysed or there is a genuine difference in the effective shape of N in the two species. In default of the former, we are obliged to assume the latter.

### Discussion

The effective shapes of non-bonded atoms in molecular crystals are the result of intermolecular forces. These forces can be considered as the sum of attractive and repulsive terms; at equilibrium, the net force is zero. The dispersion forces between molecules are always attractive and the interactions between electrons in the outer molecular orbitals are always repulsive. The polar, dipolar and multipolar forces are either attractive or repulsive depending on the signs of their component charges and their spatial distribution. To take a specific example of the relevance of intermolecular forces to effective shape, we have seen that for N in [Ni(CN)<sub>4</sub>]<sup>2-</sup> (Table 3), *b* is smaller than for N in  $-C\equiv N$  (Table 1). One might have expected a larger *b* value (greater distance of closest approach) because two complex ions carrying charges of the same sign would be expected to experience a larger repulsive force than that experienced by neutral species. However, anions are considerably more polarizable than their uncharged

counterparts and it thus seems probable that for these complex ions, attractive dispersion forces more than compensate for the increased polar forces. Similar remarks apply to the smaller  $b$  of  $[\text{Co}(\text{CO})_4]^-$ , Table 3, compared to that for  $\text{>C=O}$  of Table 1.

The results presented here have clear implications for the 'atom-atom' potential formulation widely used in lattice-energy and crystal-packing programs. First, the potential energy between non-bonded atoms cannot, in many cases, be adequately represented by a spherically symmetric force field. Second, in most applications of the atom-atom method, the potential-energy parameters which are associated with an atom are assumed to be independent of its chemical environment. Since we have presented here evidence that effective non-bonded atomic shapes are environment-sensitive, it follows that atom-atom potential-energy parameters are environment-dependent also.

Further surveys for the atoms studied here, and for others, in different chemical environments, are currently being carried out in these laboratories.

Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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## SHORT COMMUNICATION

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

*Acta Cryst.* (1985). **B41**, 279

**Structural investigations of phosphorus-nitrogen compounds. 1. The structures of the three monospiro compounds:  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_2\text{O}]\text{Cl}_4$ ,  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_3\text{O}]\text{Cl}_4$  and  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_4\text{O}]\text{Cl}_4$ . The relationship of OPO bond angles in  $\text{PO}_2\text{N}_2$  tetrahedra with  $^{31}\text{P}$  chemical shifts.** By S. R. CONTRACTOR, M. B. HURSTHOUSE, L. S. SHAW (née GÖZEN), R. A. SHAW and H. YILMAZ, *Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX and Department of Chemistry, Queen Mary College (University of London), Mile End Road, London E1 4NS, England*

(Received 3 May 1985)

#### Abstract

A printer's error is corrected. In the paper by Contractor, Hursthouse, Shaw, Shaw & Yilmaz [*Acta Cryst.* (1985). **B41**, 122-131], Fig. 9 shows the incorrect numbering for one atom. A corrected figure is given.

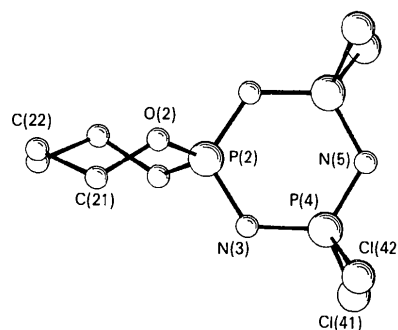


Fig. 9. Molecular diagram of (3) showing the conformation of the phosphate ring.

The correct numbering for molecule (3) is shown in Fig. 9.