SHORT COMMUNICATIONS

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Structural metrics relationships in covalently bonded organic azides

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Abstract

Geometrical parameters of covalently bonded organic azides have been analysed using X-ray structural data retrieved from the Cambridge Structural Database. The *R*NNN fragment geometry shows some important general features: (i) a preference for a *trans* C_s configuration; (ii) bending of the N—N—N unit; (iii) substantially different N—N bond lengths in the azide group. Electron-density redistribution within the covalently bonded azide group (relative to that in the isolated azide anion) promotes the capacity of the terminal azide N atom to form hydrogen bonds.

1. Introduction

This work is a part of my continuing study of the crystal space environment of certain functional groups in which I attempt to relate the intramolecular geometry of a polyfunctional entity to its hydrogen-bonding capacity. The influence of covalent bonding with metals and nonmetals on the hydrogen-bonding geometry has been established for the thiocyanate group (Tchertanov & Pascard, 1997). This study is focused on the azide group, an important building block in organic syntheses (Scriven & Turnbull, 1988, and references therein). Of topical interest, azidonucleosides [AZT (3′-azido-3′-deoxythymidine) and CS-85] have received international attention for the treatment of AIDS (acquired immune deficiency syndrome) and ARC (AIDS-related complexes) (Lin & Prusoff, 1978; Robins, 1986; Dagani, 1986; Barnes, 1986). Theoretical aspects and the electronic structure of covalent azides have been reviewed by Treinin (1971) and Kaftory (1983), and more recently by Klapötke (1997). A preliminary survey of azide groups in the solid state has been covered briefly in a review of triply bonded functional groups (Allen & Garner, 1994). The main purpose of this study is a more detailed description of the N_3 subunit geometry and the recognition of azides by donor groups based on the atomic structural coordinates of covalent organic azide derivatives retrieved from the Cambridge Structural Database (CSD; Allen & Kennard, 1993).

2. Method

Relevant structures were retrieved from the CSD (October 1998 release, 190 307 entries). Substructure search, geometry calculations and data analysis were performed *via* the CSD programs *QUEST*3*D* and *VISTA* for two different groups of compounds: (i) crystal structures containing discrete azide anions and (ii) azides covalently bonded to nonmetallic atoms (*R* = B, C, N, O, F, Si, P, S, Cl, Ar, Se, Br, Te and I). Searches were carried out for generalized fragments N1—N2—N3 and *R*—N1—N2—N3 where: (*a*) N3 terminal atoms were required to be bonded to only one atom and the central N2 atom to only two atoms, *i.e. sp* hybridization; (*b*) the N—N bonds were allowed to be single, double or triple; (*c*) atomic charges were not specified. Only structures with no reported disorder were accepted for analysis. A total of 15 entries (18 independent N1—N2—N3 fragments) for group (i) and 170 entries (232 independent *R*—N1—N2—N3 fragments) for group (ii) were retrieved for geometrical analysis. All molecules related to group (ii) were classified according to the type and the chemical nature of *R*. Structural data on azides covalently bonded to non-C atoms are very scarce; occurrences where *R* is bonded *via* I, Te, P, Si and B atoms are 4, 1, 14, 5 and 8, respectively. The remaining 200 fragments correspond to *R* groups bonded to the azide group *via* C atoms. Relevant REFCODES have been deposited.†

3. Results and discussion

As reported previously, the azide ion is linear and symmetrical, with mean values (m.v.) of the N—N—N angle of 179 (2)° and N—N bond length of 1.158 (4) Å. This agrees with the proposed resonance among the three canonical structures (I*a*)–(I*c*) (Pauling, 1960) where (I*a*) is $^{-}N{=}N^{+}{=}N^{-}$, (I*b*) is $^{--}N{-}N^{+}{\equiv}N$ and (I*c*) is $N{\equiv}N^{+}{-}N^{--}$. The covalently bonded azides mostly have a slightly bent N—N—N unit [N1—N2—N3 172.6 (2)°] and in all cases feature two distinctly different N—N bond lengths (Δ = 0.1 Å); the m.v.'s for N2—N3 and N1—N2 are 1.128 (2) and 1.222 (3) Å, respectively. The relationships in these triatomic fragments show that the triple-bond character of the terminal N2—N3 bond increases as the single-bond character of N1—N2 decreases, which may be associated with the non-uniform contributions of the limiting canonic forms, that of (2*b*) being obviously much higher than that of (2*c*) (Pauling, 1960) where (2*a*) is $R{-}N{=}N^{+}{=}N^{-}$, (2*b*) is $R{-}^{-}N{-}N^{+}{\equiv}N$ and (2*c*) is $R{-}N^{+}{\equiv}N^{+}{-}N^{--}$. Nearly all covalently bonded azides display a *trans* C_s configuration. The bond distances *R*—N1 vary from 1.31 (1) to 2.40 (1) Å depending on the nature of the atom of the *R* group actually bonded to the azide N atom, m.v.'s being 1.466 (3), 1.52 (1), 1.774 (8), 1.789 (7) and 2.22 (3) Å for C, B, P, Si and I, respectively (Table 1).

Molecules with the *R* group bonded through its C atom belong to heterogeneous chemical classes, *viz*. carbohydrates, hydrocarbons or heteronitrogen rings of different sizes. In most cases (80% or 163 occurrences) the hybridization state is

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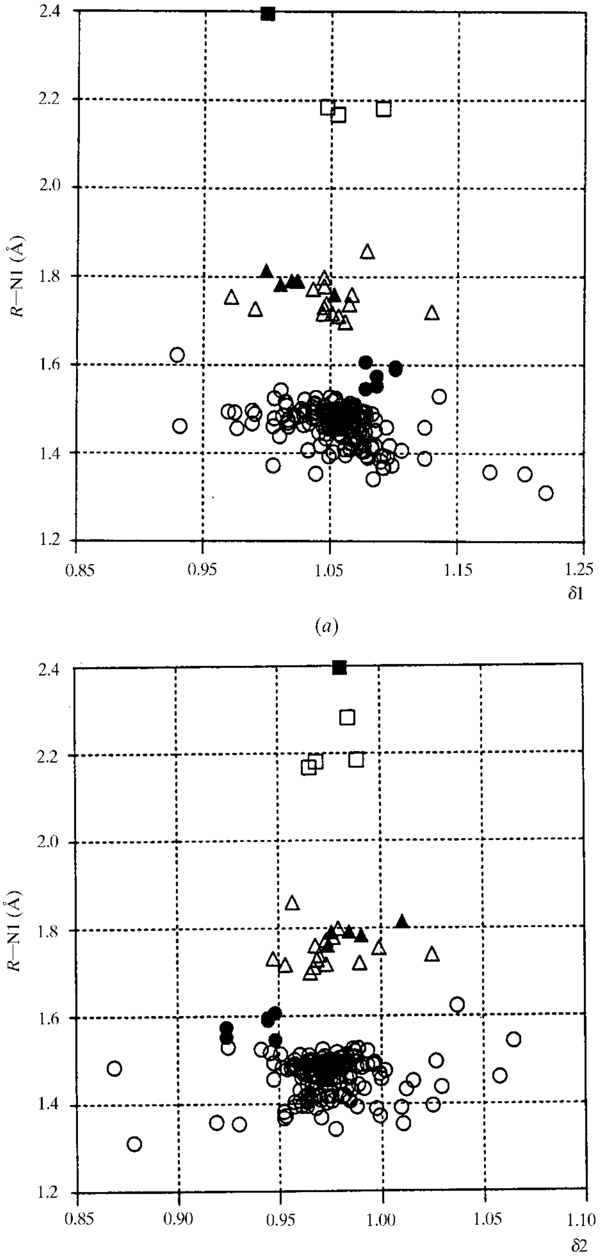
† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0550). Services for accessing these data are described at the back of the journal.

Csp^3, less frequently it is Csp^2 (18% or 35 occurrences) and only two fragments correspond to a transient carbenium ion (R_3C^+). The m.v.'s of the R1—N2 distances are 1.480 (2) Å for Csp^3 and 1.406 (5) Å for Csp^2. The bond angle R—N1—N2 does not differ for I, P, B and C; however, for Si derivatives this angle is substantially wider (Table 1). Fragments with Csp^3 and Csp^2 hybridization states were also averaged separately but do not show any statistically significant differences.



(*a*)

(*b*)

Fig. 1. Scatter plots of the distance R—N1 *versus* (*a*) δ1 and (*b*) δ2. White and black circles correspond to compounds with the azide group bonded to carbon and boron, respectively, white and black triangles correspond to compounds with the azide group bonded to phosphorus and silicon, respectively, and white and black squares correspond to compounds with the azide group bonded to iodine and tellurium, respectively.

Table 1. *Mean values of the R—N1 distance (Å) and R—N1—N2 angle (°) for the RN1N2N3 fragment*

The standard deviation of the mean is given in parentheses.

R	R—N1	R—N1—N2	N_{obs}
C (all)	1.466 (3)	115.4 (4)	200
Csp^2	1.406 (5)	115.0 (8)	37
Csp^3	1.480 (2)	115.6 (2)	163
B	1.52 (1)	116.6 (7)	8
P	1.774 (8)	117.0 (7)	14
Si	1.789 (7)	128 (1)	5
I	2.22 (3)	114 (4)	4
Te†	2.40 (1)	120 (2)	1

† One observation only. The published standard deviation is given.

To characterize the relationships between R—N1—N2—N3 bond metrics, a simple geometrical parameter, defined as $\delta = (\mathrm{N-N})_{\mathrm{cov}}/(\mathrm{N-N})_{\mathrm{anion}}$, is used as an index of the degree of N—N bond-distance variation (δ1 for N1—N2 and δ2 for N2—N3) in covalently bonded compounds relative to the dimensions of the discrete anion. Fig. 1 shows scatter plots of (*a*) δ1 and (*b*) δ2 *versus* R—N1, illustrating the difference between each of the N—N bond distances in covalently bonded azides and those in the anion. The large majority of δ1 observations are greater than 1.0, with most δ2 values less than 1; moreover, the δ1 values show larger differences from unity than the δ2 values. Covalent binding appears to lengthen N1—N2 more (δ1 = 1.03–1.10) than it reduces N2—N3 (δ1 = 0.95–1.00).

The equivalent N—N bond distances and linearity of the azide ion indicate that the most important factor in the system is the π-delocalization over the triatomic unit. On the other hand, in covalently bonded azides there is competition between resonance effects and a strong negative (anionic) hyperconjugation (Schleyer & Kos, 1983) which donates electron density from the filled σ(R—N1) orbital into the unfilled, antibonding π*(N2—N3) orbital. Negative hyperconjugation is important in both charged and neutral systems.

The structures studied are rich with hydrogen-bond donor groups (70 structures contain one or more donor groups, but in most cases the potential hydrogen-bonding partner prefers another acceptor group such as carbonyl). It was found that the terminal N atom (N3) of a covalently bonded azide participates in hydrogen bonding only in a few structures (DAHLIH, FIZDIB and VIRZUR) forming a very weak hydrogen bond with a hydroxy group (N···O ≃ 3.10, N···H ≃ 2.74 Å and N···H—O ≃ 109°). In contrast, multiple hydrogen bonding around the isolated azide anion is frequently observed: in some cases both terminal N atoms are involved in as many as four and three hydrogen bonds simultaneously (KESVOT). A similar, but not so drastic, reduction of hydrogen-bond accepting ability was also observed in the SCN system. The hydrogen-bond accepting ability of the terminal atoms varies from very good for the SCN anion to good in RNCS and to relatively poor in RSCN (Tchertanov & Pascard, 1997). Here the substituent effect on the SCN unit gives rise to a variation of the S—C bond length alone in both thiocyanato and isothiocyanato (RSCN and RNCS, R = C, B, P, Si and As) derivatives: 1.547 (5) Å in RNCS, 1.624 (4) Å in the anion and 1.683 (5) Å in RSCN. Other metrics (N—C and S–C—N) did not show any significant variations.

4. Conclusions

The structural data for covalent azides available in the CSD have made possible the analysis of their covalent and non-covalent interactions. This paper reports a study of the azide derivatives which considers the effect of substituents on the azide unit. The most important result concerning the substituent influence is a redistribution of electron density within the azide group which decreases its capacity for hydrogen bonding.

Recently, the first X-ray study of a protein complex with AZT was reported (Xu *et al.*, 1997). The complex of azidothymidine diphosphate with nucleoside diphosphate (NDP) kinase was investigated crystallographically in an attempt to understand why NDP kinase is so inefficient in activating AZT in comparison with natural substrates. It was concluded that the dominant factor in explaining the low activity of NDP kinase on AZT was the absence of hydrogen bonding by the azido group. The above results are in good accordance with these observations.

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