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Bond length relationships in diazo and diazonium compounds.

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Abstract

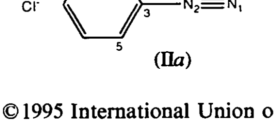
Geometrical data for 52 instances of the C—N≡N substructure have been retrieved from the Cambridge Structural Database. A scatterplot of the N≡N bond length (range 1.078–1.146 Å) *versus* the C—N bond length (range 1.278–1.450 Å) shows a strong negative correlation (linear correlation coefficient = −0.846): a decrease in N≡N triple-bond character is directly correlated with increasing double-bond character of C—N. Three discrete chemical subgroups can be identified in the dataset: benzenediazonium compounds, α-diazoketones and diazoalkanes with mean N≡N/C—N bond lengths of 1.093 (2)/1.394 (6), 1.115 (3)/1.328 (5) and 1.133 (3)/1.301 (8) Å, respectively.

Introduction

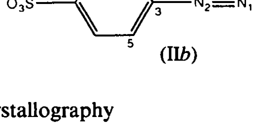
The formal chemical substructure C—N≡N occurs in two classes of organic compounds: diazo compounds (I) and diazonium cations (II) (Sorriso, 1978). Diazo compounds (I) can be represented by resonance hybrids (I*a*) and (I*b*), where (I*b*) is predominant when the negative charge on C can be delocalized. Thus, the α-diazoketones (III) are stabilized (*via* contributions from IIIc) by comparison with the diazoalkanes (IV), where hybrid (IV*a*) makes a significant contribution to the resonance structure. The diazonium cation (II) is stabilized by conjugation with aromatic π-systems and exists in the fully ionic form (II*a*) or the zwitterionic form (II*b*). The $-\mathrm{N}^{+}{\equiv}\mathrm{N}$ system is isoelectronic with dinitrogen and we would expect to observe a short, formally triple N≡N bond. Thus, in moving from the diazonium compounds (II), through the α-diazoketones (III) to the diazoalkanes (IV) we would expect to observe an increase in the N≡N bond length ($d_{\rm NN}$) and a concomitant decrease in the C—N bond length ($d_{\rm CN}$) in C—N≡N systems. A preliminary survey of C—N≡N geometry, incorporated in a recent review of triply-bonded functional groups (Allen & Garner, 1994), indicated systematic variations of $d_{\rm NN}$ with $d_{\rm CN}$ associated with chemical environment. In this short communication, we report a more complete analysis of C—N≡N geometry based on a larger dataset retrieved from the Cambridge Structural Database (CSD, Allen *et al.*, 1991).

$$\mathrm{C{=}\overset{+}{N}{=}N^{-}} \longleftrightarrow \mathrm{{}^{-}C{-}\overset{+}{N}{\equiv}N}$$

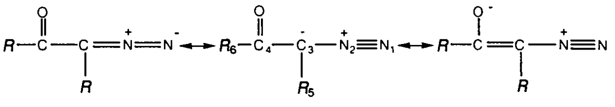
(I*a*) (I*b*)



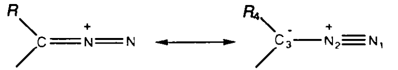
(II*a*)



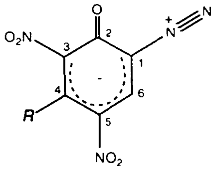
(II*b*)



(III*a*) (III*b*) (III*c*)



(IV*a*) (IV*b*)



(V) *R* = H
(VI) *R* = Cl

Methodology

Version 5.5 (April 1993, 109 992 entries) of the CSD system was used for substructure search, geometry calculations and data analysis *via* the programs *QUEST*3D and *GSTAT* (CSD User Manual, 1992). Because of difficulties in the representation of the C—N≡N fragment in the chemical connection tables of the CSD, searches were carried out for a generalized fragment $C_3{\sim}N_2{\cong}N_1$ where: (*a*) the total coordination of N_1 was required to be unity and that of N_2 was required to be two, (*b*) the $N_1{\cong}N_2$ bond was allowed to be triple or double, (c) the $N_2{\sim}C_3$ bond was allowed to be single or double, (*d*) atomic charges were not specified, *i.e.* any values were accepted, and (*e*) the hybridization (total coordination) of C_3 was not specified. These specifications, particularly the terminal nature of N_1, were sufficient to retrieve all available diazo and diazonium derivatives. Edits of the CSD are now in hand to improve the consistency of the two-dimensional chemical representations as a result of this study.

Secondary search constraints were imposed by use of the CSD bit-screen mechanism (CSD User Manual, 1992) to locate only those entries that had: (*a*) error-free atomic coordinates following CSD check procedures, (*b*) no reported disorder in the crystal structure, (*c*) a crystallographic R factor ≤ 0.13 and (*d*) were classified as 'organic' compounds within CSD definitions. A total of 46 entries (43 with $R \leq 0.010$) yielded 52 independent instances of the C—N≡N fragment: 19 instances of (II), 23 instances of (III), six instances of (IV) and four instances that could not readily be classified in chemical categories (II–IV). Relevant CSD reference codes are given in

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Table 1. *CSD reference codes for the crystal structures used in this analysis*

Full literature citations have been deposited. The classification of structures marked (+) is discussed in the text.

Benzenediazonium compounds (II)			
AZOSUL01	BIBVEN	CIYZEP	FAHDOH
AZPOSM	BOSPUU	CNAPZS	MORBDZ
BAXZAB	BZDIZC	CXNPZB	
BDAZAC	CAZCHO	DARWEY	
BDAZCZ	CEWJOD	DUJTUX	
α-Diazoketones (III)			
AZASER11	DIAZNE	GETFIU$^+$	SOJCEZ
AZBUTO	DUCWAZ	GETFOA$^+$	VIRBON
AZCYHO	FATZEF	GEYZIT	VUCSOB
BEFVEN	FAYMAT	SAFKAL	ZAZBAD
BOAZME	FAYMEX	SAWGOM	
DAZCAM	FENYIG	SIXDAE	
Diazoalkanes (IV)			
DAZFLU10	PSIAZM	TAJXEH	VAYFIK
Unclassified			
DAZIND$^+$	DUMJOK$^+$	JOXJOV$^+$	

Table 1 and full literature citations have been deposited.* The geometrical parameters d_{CN}, d_{NN} and the four valence angles at N_2, C_3 in (II–IV) were calculated for all 52 examples of the fragment.

Results and discussion

Despite the narrow range of d_{NN} (0.068 Å), the scatterplot of d_{NN} *versus* d_{CN} (Fig. 1) shows a strong negative correlation. The slight curve exhibited in Fig. 1 is typical of bond length–bond number relationships in triatomic species (see *e.g.* Dunitz, 1979): the double-bond character of C—N increases (almost linearly over the narrow bond length ranges) as the triple-bond character of N≡N decreases. Simple linear regressions based on the data of Fig. 1 yield predictive equations of the form

$$d_{NN} = 1.568\,(41) - 0.341\,(30)\,d_{CN}$$

$$d_{CN} = 3.67\,(20) - 2.10\,(19)\,d_{NN},$$

where the figures in parentheses are standard errors and the statistical significance of the linear equations is >99.5%. Fig. 1 also distinguishes the three main types of C—N≡N compounds (II–IV). The two major subgroups (II) and (III) also reflect the strong negative bond length correlation within themselves, with $C(d_{NN}, d_{CN}) = -0.50$ for (II) and -0.66 for (III).

Mean geometrical parameters for subgroups (II–IV) are collected in Table 2. The N≡N distances in benzenediazonium compounds (II) lie at the shorter end of the d_{NN} range. The mean value of d_{NN} at 1.093 (2) Å is almost identical to the 1.097 Å observed by Stoicheff (1954) for dinitrogen, and is significantly shorter than mean values of d_{NN} for (III) and (IV). The mean d_{CN} value [1.394 (6) Å] is very considerably longer in (II) than in the other two subgroups. This C(aromatic)—N distance lies between the values (Allen *et al.*, 1987) for C_{ar}—$N(Csp^3)_2$ systems in which N is sp^2-planar [1.371 (3) Å] or sp^3-pyramidal [1.426 (2) Å]. These and other comparisons (Allen & Garner, 1994) indicate that the C_{ar}—N bond in benzenediazonium compounds (II) is essentially single but is slightly foreshortened by the conjugative interactions that stabilize these systems relative to their highly reactive alkyl analogues. The other important geometrical feature of (II) is the ipso angle in the phenyl group (θ_{435} in Table 2), which is enlarged to the high value of 124.5 (4)° as a result of the very strong electron-withdrawing properties of the diazo group (Domenicano & Murray-Rust, 1976).

The α-diazoketones (III) have mid-range d_{NN} values [mean d_{NN} = 1.115 (3) Å] with a mean d_{CN} of 1.328 (5) Å, a value that is much longer than a formal C=N double bond [1.279 (1) Å; Allen *et al.*, 1987] but is comparable to C≃N bond lengths in delocalized systems such as pyrazole [1.329 (3) Å]. Further, the mean C—C(=O) bond in (III) at 1.436 (3) Å is much shorter than the analogous bond in conjugated C=C—C(=O) systems [1.464 (1) Å; Allen *et al.*, 1987], while the mean keto C=O bond is 1.221 (2) Å, slightly longer than the mean for non-conjugated >C=O systems [1.210 (1) Å], but comparable to the values of 1.221 (1)–1.222 (1) found in C_{ar}—C=O, C=C—C=O and in benzoquinones. The configuration at C_3 is almost planar (sum of mean angles = 359.2°), but the (O=)C—C—R_1 angle is expanded to a mean of 124.9 (14)°, almost identical to the analogous ipso angle in (II).

There are, however, two α-diazoketone stuctures that do not fit this general description: the diazophenols (V) and (VI) (GETFIU, GETFOA; Lowe-Ma, Nissan, Wilson, Houk &

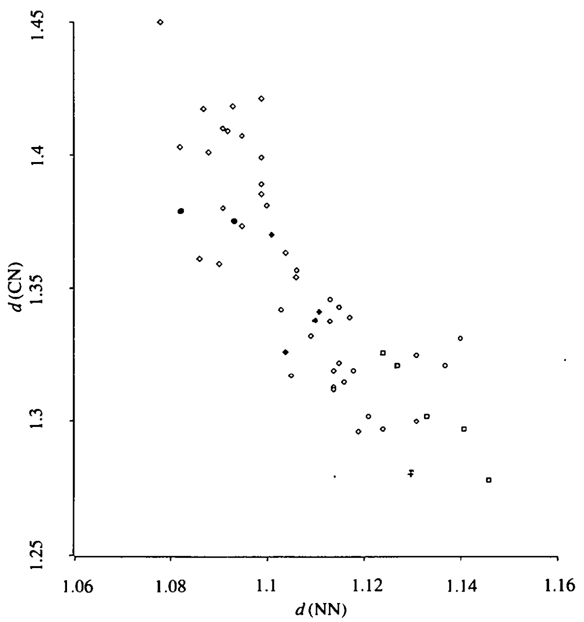

Fig. 1. Plot of the C—N distance [*d*(CN) in Å] *versus* the N≡N distance [*d*(NN) in Å]. Values for diazonium compounds (II) are shown as open diamonds. Values for α-diazoketones (III) are shown as open circles, except for the diazophenols (V, VI) where filled circles are used. The open squares represent diazoalkanes (IV), filled diamonds represent unclassified fragments (see text) and the + symbol represent gas-phase results (Sheridan, 1962) for diazomethane.

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* Full literature citations for the 46 CSD entries have been deposited with the IUCr (Reference: HA0129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

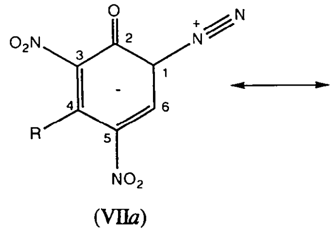
Table 2. *Mean bond lengths* (Å) *and valence angles* (°) *observed in crystal structures of benzenediazonium compounds* (II), *α-diazoketones* (III) *and diazoalkanes* (IV)

Overall mean values are also given for appropriate parameters. E.s.d.'s of mean values are in parentheses, N_{obs} is the number of observations.

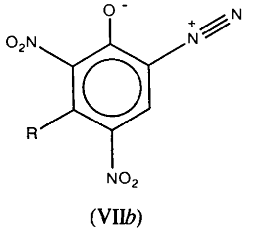
Parameter	(II)	(III)	(IV)	Overall
d_{NN}	1.093 (2)	1.115 (3)	1.133 (3)	1.109 (2)
d_{CN}	1.394 (6)	1.328 (5)	1.301 (8)	1.350 (6)
d_{CC}	1.393 (3)*	1.436 (3)	–	–
d_{CO}	–	1.222 (2)	–	–
θ_{123}	177.0 (7)	177.2 (3)	178.5 (6)	177.4 (3)
θ_{234}	117.7 (4)*	116.4 (7)	122.8 (14)	–
θ_{235}	[117.7 (4)]	117.9 (19)	122.5 (19)	–
θ_{435}	124.5 (4)	124.9 (14)	114.6 (30)	–
N_{obs}	19	23	6	52

* Averaged over $2N_{obs}$ symmetry equivalents.

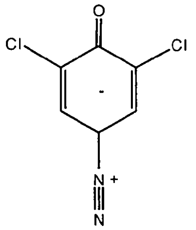
Wang, 1988). Both structures have short d_{NN} [1.082 (5) in (V), 1.093 (4) Å in (VI)] and long d_{CN} [1.379 (5) in (V), 1.375 (4) Å in (VI) distances] by comparison with other α-diazoketones. Further, the cyclic C—C(=O) bonds in (V) and (VI) [C_1—C_2, C_2—C_3 = 1.446–1.460, mean = 1.454 (3) Å] are long and the other ring bonds show considerable variability: C_4—C_5 is long at 1.402 (3) in (V) and 1.429 (4) Å in (VI), C_1—C_6 is shorter [1.376 (2) in (V), 1.388 (3) Å in (VI)], and C_3—C_4 and C_5—C_6 shorter still in the range 1.354–1.367 Å. On the basis of the X-ray results, ^{13}C NMR spectroscopy and MO calculations, Lowe-Ma, Nissan, Wilson, Houk & Wang (1988) conclude that representations (V) and (VI), as a diazonium cation with a negative charge delocalized over the ring as shown are the most appropriate. There is no doubt that the ring bond lengths are more closely consistent with the quinonoid representation (VII*a*) than with the phenolate representation (VII*b*), a conclusion that is supported by the short >C=O bond lengths of 1.221 (2) and 1.231 (3) Å in (V) and (VI), respectively. We find a mean >C—O$^-$ bond length of 1.281 (3) Å for the 35 phenolates ($R \leq 0.100$) available in the CSD. Thus, (V) and (VI) are clearly related to the quinonoid structure observed by Presley & Sass (1970) for CAZCHO (VIII) and all three structures should properly be classified as diazonium compounds.



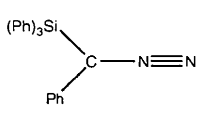
(VII*a*)



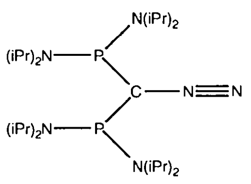
(VII*b*)



(VIII)



(IX)



(X)

The six diazoalkane fragments (IV) yield a mean d_{NN} distance of 1.133 (3) Å, longer than the N≡N distance in azides [1.124 (3) Å; Allen *et al.*, 1987]. The mean d_{CN} distance is correspondingly short at 1.301 (8) Å, much closer to the 1.279 (1) Å mean for C=N bonds (Allen *et al.*, 1987). Resonance hybrid (IV*a*) makes a very significant contribution to the ground state structures of diazoalkanes. This is particularly true for (IX) (PSIAZM; Glidewell & Sheldrick, 1972) and (X) (VAYFIK; Menu *et al.*, 1989), which have the shortest d_{CN} [1.281 (8) and 1.278 (6) Å, respectively] in the whole dataset. The diazo group of (IX) can delocalize negative charge to the single phenyl substituent, but this is not possible in (X) and, as a result, this structure has the largest contribution from (IV*a*) and the longest d_{NN} at 1.146 (5) Å of all the structures surveyed. The limited X-ray data so far available for diazoalkanes are in general agreement with gas-phase results for diazomethane [d_{NN} = 1.130, d_{CN} = 1.280 Å; Sheridan, 1962].

Four fragments were not immediately classifiable, on chemical grounds, into the structural classes (II–IV). This group comprises two independent diethoxyvinyldiazonium groups (hexachloroantimonate counter-ion) from JOXJOV [d_{CN} = 1.326 (15), 1.370 (16); d_{NN} = 1.101 (15), 1.104 (15) Å; Glaser, Chen & Barnes, 1992], a diazoindazole [DAZIND; d_{CN} = 1.338 (3), d_{NN} = 1.110 (3) Å; Leban, Stanovnik & Tisler, 1978] and a diazothiapyran [DUMJOK: d_{CN} = 1.341 (8), d_{NN} = 1.111 (6) Å; Fox, Chen & Luss, 1986]. Of these, JOXJOV is the first aliphatic diazonium salt studied crystallographically (at 173 K) and experimental procedures were not simple. Thus, the two independent d_{CN} values differ by 0.044 Å, but this difference is within a 3σ limit. Despite the limited precision, the d_{NN} values fall clearly within the expected range for diazonium compounds (II). The other two compounds (DAZIND, DUMJOK) have geometries that place them clearly in the 'α-diazoketone' (III) area of Fig. 1. This is consistent with their chemical structures which permit a stabilizing charge delocalization over the bonded ring system.

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Oxygen-induced structural change of the tetragonal phase around the tetragonal–cubic phase boundary in ZrO_2–$YO_{1.5}$ solid solutions. Addendum.

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Abstract

Primary diffraction data for this paper [Yashima, Sasaki, Kakihana, Yamaguchi, Arasi & Yashimura (1994). *Acta Cryst.* B**50**, 663–672] have been deposited with the IUCr (Reference: OH0040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All relevant information is given in the *Abstract*.