Some Comments on Carbon-Hydrogen and Nitrogen-Hydrogen Distances Assumed in, and Determined from, Recent X-Ray Diffraction Studies on Inorganic Complexes

Sir:

The purposes of the present article are as follows. (1) To remind readers of this journal, particularly structural inorganic chemists, of the anomalously short distances found by X-ray diffraction methods, for bonds involving hydrogen atoms. (2) To point out the wide range of carbon-hydrogen and nitrogen-hydrogen distances that have been used in producing so-called "calculated hydrogen atom positions" in recent articles describing X-ray diffraction studies. (3) To provide a compilation of recent X-ray diffraction studies on inorganic molecules in which the positions of hydrogen atoms have been meaningfully refined, thereby providing optimized C-H and N-H distances which may be used as valid, rather than arbitrary, criteria for assigning idealized positions to hydrogen atoms which are ill-behaved during attempted refinement procedures.

It is generally understood (*cf.* ref 1) that different techniques for measuring a given interatomic distance will not, necessarily, yield identical values. Thus, while techniques such as neutron diffraction, electron diffraction, and molecular spectroscopy give essentially equivalent results for an internuclear distance, bond distances involving hydrogen as measured by X-ray diffraction techniques are systematically shortened. This discrepancy arises because the "X-ray determined" bond length is a measure of the distance between the centroids of electron density of the two atoms concerned, and the centroid of electron density around a covalently bonded hydrogen atom is not coincident with its nuclear position but is displaced significantly in the direction of the hydrogen-(other atom) σ bond.

Stewart, Davidson, and Simpson[2] have indicated on theoretical grounds that the use of free-atom spherically symmetric scattering factors for hydrogen will result in reductions (relative to the true internuclear separation) of approximately 0.14 Å for an H-H bond and approximately 0.09 Å for C-H, N-H, and O-H bonds determined from X-ray diffraction studies. Hamilton and Ibers[3] have commented on this same problem.

We may note at this point that typical *internuclear* distances are C-H = 1.08 Å[4] and N-H = 1.01 Å[5].

In order to avoid a truly Herculean task, the present survey was limited to crystallographic papers appearing in *Inorganic Chemistry*, Vol. 11, 1972 [hereafter referred to as INORG-72], and to structural studies performed recently in my own laboratory.

Of approximately 100 crystallographic papers appearing in INORG-72, 2 were neutron diffraction studies, 12 reported species containing no hydrogen atoms, and in 22 cases the authors did not include hydrogen atom contributions to the calculated structure factor amplitudes. Other authors provided only vague descriptions of their location or inclusion of hydrogen atoms, while several used hydrogen atom positions determined from difference-Fourier syntheses.

Table I. Carbon-Hydrogen Distances Used for Calculating Hydrogen Atom Positions[a]

Dist, Å	Freq of citation	Dist, Å	Freq of citation
1.10	1[b]	1.00	11
1.09	3	0.98	2
1.084	1	0.97	1
1.08	8	0.95	2
1.06	1	0.90	3[c]

[a] All data taken from INORG-72. [b] A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, 11, 3021 (1972). [c] *E.g.*, P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, 11, 3040 (1972).

Table II. Values for C-H Distances Obtained *via* Least-Squares Refinement [Inorganic Species]

Complex	Range, Å	No. of measurements	Mean value, Å	Ref
$[-CH_2NH_2\cdot BH_3]_2$	0.89 (4)–0.98 (4)	2	0.94	6
$Ni(C_7H_{14}N_4O_2)\cdot 3H_2O$	0.94 (3)–1.07 (4)	10	0.99	7
$Pd(S_4C_4H_4)_2$	0.84 (14)–1.03 (11)	4	0.95	8
$CuBr_2(C_7N_2H_{10})$	0.80 (14)–1.17 (10)	10	0.98	9
$CuBr(N_3)[NH(CH_2CH_2NEt_2)_2]$	0.80 (7)–1.18 (6)	28	0.97	10
$[C_5H_5Fe(CO)_2]_2SO_2$	0.83 (4)–0.97 (4)	10	0.92	11
$(C_7H_6CH_2)Fe(CO)_3$	0.86 (6)–1.15 (7)	8	0.98	12
$(C_5Me_5RhCl)_2HCl$	0.77 (8)–1.09 (11)	15	0.91	13
$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$	0.76 (2)–1.10 (6)	26	0.91	14
$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$	0.85 (4)–1.09 (4)	13	0.96	15
$C_5H_5Fe(CO)_2\cdot C_4H_7C_2(CN)_4\cdot$	0.86 (2)–1.05 (3)	24	0.95	16
$(pentalene)_2Fe$	0.81 (6)–1.05 (5)	12	0.95	17
$Cr(CO_2CH_2NH_2)_2\cdot H_2O$	0.90 (2)–1.03 (2)	6	0.96	18

Table I summarizes the carbon-hydrogen distances *assumed* by the authors of 33 papers who described their method of positioning hydrogen atoms in calculated positions. As can readily be seen, these "idealized" distances range from 0.90 to 1.10 Å—a variation of 20%; many authors clearly realize that a reduced C-H distance is preferable; a significant number, however, cling to the use of the *invalid* spectroscopic value of ~1.08 Å. The systematic errors thereby introduced are small, but it is clearly desirable to have, conveniently available, a C-H distance that truly represents the distance between *electron density maxima* of mutually bonded carbon and hydrogen atoms. Table II summarizes some values obtained for C-H distances, following the refinement of hydrogen atom parameters. These values are principally from INORG-72[6-10] and from results obtained in my laboratory.[11-17]

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(1) *Chem. Soc., Spec. Publ.*, No. 18, 4-8 (1965).

(2) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(3) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968; see particularly pp 63-66.

(4) From *Chem. Soc., Spec. Publ.*, No. 18, S18s (1965), C-H distances are 1.094 Å in CH_4, 1.096 ± 0.005 Å in X-CH_3 species, 1.073 ± 0.005 Å in XX'-CH_2 species, 1.070 ± 0.007 Å in XX'X"CH species, and 1.084 ± 0.005 Å for C(aromatic)-H.

(5) From *Chem. Soc., Spec. Publ.*, No. 18, S7s (1965), N-H = 1.0124 Å in NH_3 and 0.995 ± 0.007 Å in $CO(NH_2)_2$.

(6) H.-Y. Ting, W. H. Watson, and H. C. Kelly, *Inorg. Chem.*, 11, 374 (1972).

(7) R. M. Lewis, G. H. Nancollas, and P. Coppens, *Inorg. Chem.*, 11, 1371 (1972).

(8) K. W. Browall, T. Bush, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, 11, 1800 (1972).

(9) V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 1826 (1972).

(10) R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 11, 3044 (1972).

Table III. Nitrogen-Hydrogen Distances Used in Calculating Hydrogen Atom Positions[a]

Dist, Å	Freq of citation	Dist, Å	Freq of citation
1.13	1[b]	0.95	1
1.01	2	0.90	2[c]
1.00	2		

[a] All data from INORG-72. [b] J. E. Fergusson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, **11**, 1662 (1972). [c] See, *e.g.*, J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 1420 (1972).

Average C-H distances range from 0.91 to 0.99 Å. The overall optimal C-H (X-ray) distance is 0.95 Å, the experimentally determined contraction from the true internuclear separation being 0.13 Å.

Table III summarizes the situation as regards *assumed* N-H distances. Again, the various assumed values differ (by *more* than 20%!). Only a few N-bonded hydrogens had been refined in the papers surveyed (see ref 6, 7, 9, 10, 18, 19). As shown in Table IV, mean experimentally-determined N-H distances range from 0.82 to 0.95 Å. The optimal N-H (X-ray) distance appears to be ~0.87 Å, representing a contraction of ~0.14 Å from the true internuclear separation.

Table IV. Values for N-H Distances Obtained by Least-Squares Refinement

Complex	Range, Å	No. of measurements	Mean value, Å	Ref
$[-CH_2NH_2 \cdot BH_3]_2$	0.84 (3)-0.86 (4)	2	0.85	6
$CuBr_2(C_7N_2H_{10})$	0.87 (11)-0.89 (7)	2	0.88	9
$Ni(C_7H_{14}N_4O_2) \cdot 3H_2O$	0.80 (3)-0.92 (4)	4	0.87	7
$CuBr(N_3)[HN(CH_2CH_2NEt_2)_2]$	0.95 (7)	1	0.95	10
$Cr(CO_2CH_2NH_2)_3 \cdot H_2O$	0.81 (2)-0.92 (2)	6	0.88	18
$(NH_4)[VO(O_2)_2(NH_3)]$	0.81 (4)-0.83 (9)	2[a]	0.82[a]	19

[a] Does not include N-H distances within the NH_4^+ ion.

Finally, it should be admitted that more precise C-H and N-H distances can be determined from X-ray diffraction studies of simple organic molecules. However, a secondary objective of this article is to convince the skeptic that the refinement of positional (and thermal) parameters of hydrogen atoms can be a meaningful procedure and leads to self-consistent results even in the presence of heavy atoms (*e.g.*, first- and second-row transition metal atoms).

A Caveat. While hydrogen atoms fixed in "calculated positions" with C-H = 0.95 Å or N-H = 0.87 Å provide the best description of the electron density distribution, these hydrogen atom positions should be used in other computational procedures with due regard to their limitations. For example, we may consider their use in the calculation of *inter*molecular distances. A computed H· · ·H contact can vary from being precisely correct (in the fortuitous case where two X-H bonds are parallel with H atoms lying precisely above one another) or can be systematically *elongated* by as much as ~0.26 Å (in the event of a linear X-H· · ·H-X contact).

For accurate intermolecular distances, and for other procedures requiring data on *nuclear* positions, C-H and N-H distances should be redefined as their true internuclear values.

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