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THE IMPORTANCE OF NON-BONDED INTERACTIONS IN AMIDE STRUCTURES

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Abstract—Explanations for the variations of bond lengths and bond angles in terms of conjugation, hyperconjugation, hybridization and non-bonded repulsions have been reviewed. Non-bonded repulsion appeared to offer the best explanation for exceptionally long C—C bonds in the ammonium salts of oxalic and oxamic acids. To apply a rigorous test to this theory, the various known amide structures were compared with theoretical structures obtained using Bartell's "hard-sphere" model and within the limits of error extremely good agreement was obtained. From this it was inferred that non-bonded repulsions are of prime importance in determining molecular geometry and the influence of hybridization, conjugation or hyperconjugation would appear to be small. Conversely the degree of conjugation or hyperconjugation cannot be deduced from bond lengths.

Two of the most widely held concepts in chemistry are that co-valent bond radii are constant and additive and interatomic distances depend on bond order. This point is well illustrated by two examples from highly recommended undergraduate texts. First Morrison and Boyd[1] in a discussion of the existence of hyperconjugation in propylene state that "consistent with partial double-bond character the C—C single bond in propylene is 1·50 Å long as compared to 1·54 Å for a pure single bond". Secondly Cotton and Wilkinson[2] in a discussion of the structure of P_4O_{10} claim that "the twelve P—O distances between phosphorous atoms and shared oxygen atoms are 1·62 Å which is about the P—O single bond distance, but the other four apical P—O distances are only 1·39 Å and indicate considerable *pπ–dπ* double bonding." In both these cases double bond character is assumed on the basis of bonds being shorter than expected. Yet it is implicit in this assumption that covalent radii are constant and additive.

Bond order–bond length relationship

Historically these ideas are based on the work of Huggins,[3] Sidgwick,[4] and Pauling[5] which led to the formulation of a comprehensive table of atomic radii by Pauling and Huggins.[6] This data has been refined over the years but the modern values[7] are still widely used to provide evidence of bond shortening. It was also recognized that the observed interatomic distances could also provide information on bond type and Pauling *et al.*[8] constructed a curve showing the dependence of C—C distances on the relative degree of multiple bond character. This curve has subsequently been modified[9] but the essential principle that a specific bond length can be correlated with a certain degree of multiple bond character remains the same. Simultaneously it was observed that C—C single bonds adjacent to multiple bonds were shorter than the C—C bond in diamond. The bond length–bond character relationship required an increase in the double bond character of the C—C bond and to provide an explanation Pauling *et al.*[10] developed the ideas of conjugation and hyperconjugation and this approach for explaining shortening of bond lengths is still widely accepted.

Hybridization theory

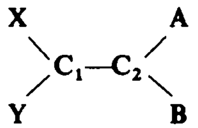
A criticism of Pauling's bond length–bond character curve is that insufficient account has been taken of changes in hybridization. It can be argued that with increasing *s*-character a C—C bond should be shorter since the 2*s* atomic orbital of carbon has a smaller mean radius than the 2*p* atomic orbitals. This led Coulson[11] to conclude that conjugation and hyperconjugation only contributes to half the observed shortenings of C—C bonds adjacent to multiple bonds, the other half being due to the change in hybridization of the C atom.

A more extreme viewpoint has been taken by Brown[12] and Dewar and Schmeising[13] amongst others, who interpret the shortening entirely in terms of changes of hybridization and claim there is no necessity to introduce hyperconjugation.

Non-bonded interaction

A very different approach (based on a scheme of Pitzer and Catalono[14]) has been put forward by Bartell,[15] who argues that non-bonded repulsions between any two atoms bonded to a given C atom strongly influence the molecular structure.

Thus for a hypothetical molecule:



the C—C bond length is very much affected by the repulsive forces X–A, Y–B, X–C_2, A–C_1, etc. These repulsive forces will be less in a molecule such as methylacetylene compared to ethane, where three H atoms are attached to each C atom. Consequently the C—C bond in ethane would be expected to be longer than the C—C bond in methylacetylene. The basic idea was originally put forward by Konn, *et al.*[16] but Bartell endeavoured to put it on a far more quantitative level than hitherto. As a first simple approximation he used a "hard sphere" model and proposed that bond angles, at least about trigonal C atoms, are largely determined by steric interference between attached groups. "Hard sphere" radii analogous to Pauling's intermolecular van der Waals' radii, were assigned to the atoms H, C, N, O, F and Cl and the bond angles predicted for twenty two substituted ethylene and carbonyl derivatives. The agreement between measured and predicted angles was sufficiently good for Bartell to claim that non-bonded repulsions were more important than the effects of hybridization, conjugation or hyperconjugation in governing bond angles and bond distances.

Bright Wilson[17] was extremely critical of these ideas and pointed out that the "hard sphere" radii were obtained from the same molecules which were subsequently used as a check for the theory. If these radii were applied to other independent molecules the calculated bond angles were not so impressive. Consequently in

Bright Wilson's opinion conjugation and hyperconjugation offer the most plausible explanation for the shortening of carbon–carbon bonds adjacent to multiple bonds.

Long carbon–carbon bonds

Until very recently the theoretical problem has been to explain the observed shortening of a single bond when it is adjacent to a multiple bond. However, the problem has now become more complex. Highly accurate X-ray studies of ammonium oxalate[18] and ammonium oxamate[19] have indicated that the central C—C bond although adjacent to carbonyl groupings is actually longer than the C—C bond in diamond. Conjugation and hybridization approaches would both suggest a bond length shorter than in diamond and steric repulsion would appear to offer the best explanation.

TABLE 1. PREDICTIONS OF BOND ANGLES*

Molecule	Angle	Obs.	Calc.	Δ
CH_3CHO†	CCO	123° 55′	123° 10′	0° 45′
	OCH	118° 36′	124° 24′	5° 48′
	CCH	117° 29′	122° 27′	5° 2′
CH_3CFO	CCO	128° 21′	125° 53′	2° 28′
	OCF	121° 21′	123° 14′	1° 53′
	CCF	110° 18′	110° 54′	0° 36′
CH_3CClO	CCO	127° 5′	126° 47′	0° 18′
	OCCl	120° 16′	120° 42′	0° 26′
	CCCl	112° 39′	112° 32′	0° 7′
CH_3CCNO	H_3CCO	124° 3′	121° 37′	2° 26′
	OCCN	120° 58′	123° 23′	2° 34′
	CCCN	114° 59′	115° 0′	0° 1′
CH_2CHCl	CCCl	122° 18′	121° 42′	0° 36′
	CCH	123° 49′	127° 2′	3° 3′
	HCCl	113° 53′	111° 15′	2° 38′
HFCO	FCO	122° 7′	122° 40′	0° 33′
	HCO	129°	122° 50′	6° 10′
	HCF	108°	114° 30′	6° 30′
H_2CCHCH_3	CCC	124° 18′	122° 52′	1° 26′
	CCH	119° 0′	124′ 58′	5° 58′
	HCC	116° 42′	112° 10′	4° 32′
H_2CCCl_2	CCCl	123° 10′	123° 21′	0° 7′
	ClCCl	113° 40′	113° 29′	0° 11′
Root-Mean-Square				3·2°

* Table 1 has been taken in its entirety from a paper by E. Bright Wilson, *Tetrahedron* **17**, 191 (1962).

† The angles quoted for CH_3CHO all refer to the aldehyde group.

In view of this it is worth looking at the criticism of these ideas again. Bright Wilson claimed that the steric approach is untenable because applying Bartell's method to calculating the bond angles in eight molecules the root mean square error in the calculated angles is 3·2° (Table 1) which he regards as excessively high. However, the largest errors are all for angles involving H atoms. If it is assumed that it is difficult to assign a reliable "hard sphere" radius for hydrogen (and this is a reasonable assumption if the difficulties of obtaining a suitable value for the intermolecular van der Waal's radius for hydrogen are considered) and only those angles involving atoms other than hydrogen are considered, the root mean square error is 1·3°. Since the precision in the measurement of the angles is ±0·5° this represents very good agreement and tends to support Bartell's case rather than invalidate it.

Hard sphere model applied to amides

In view of these results, Bartell's ideas are worth further examination. Obviously the "hard sphere" model is an approximation and is related to the electron density about an atom. Polarization of charge will affect the electron density and H atoms

TABLE 2. BOND LENGTHS IN AMIDO-GROUPS (IN Å)

Molecule	C—C	C—N	C—O
Formamide[a]	—	1·343	1·243
Ammonium Oxamate[a]	1·564	1·324	1·248
Sorbamide[a]	1·478	1·343	1·261
Thioacetamide[a]	1·494	1·324	1·713*
Urea[a]	—	1·356	1·276
Thiourea[a]	—	1·340	1·720*
Triuret[a]	—	1·318	1·233
	—	1·325	1·242
Monofluoroacetamide[a]	1·533	1·319	1·254
Ethyl Carbamate[a]	—	1·349†	1·223†
	—	1·341‡	1·219‡
Picolinamide[a]	1·515	1·330	1·241
Oxamide[b]	1·542	1·315	1·243
Succinamide[b]	1·512	1·333	1·238
Hydroxyurea[b]	—	1·336	1·253
Difluoroacetamide[b]	1·580	1·288	1·221
Formamide[c]	—	1·300	1·255
Acetamide[c]	1·505	1·334	1·260
Glutaramide[c]	1·52	1·34	1·22
Suberamide[c]	1·522	1·322	1·248
Adipamide[c]	1·49	1·33	1·23
m-Hydroxybenzamide[c]	1·501	1·302	1·247
Nicotinamide[c]	1·52	1·34	1·22
Hydroxyurea[c]	—	1·325	1·265
Benzamide[c]	1·53	1·33	1·24
6-Amido-pyridazone[c]	1·46	1·33	1·25
Range	1·460–1·580	1·288–1·356	1·220–1·276

* C—S bond lengths (in Å). † Measured at 25°C. ‡ Measured at −105°C.

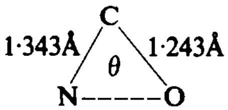
[a] Refs to be found in Table 3. [b] Refs to be found in Table 4. [c] Refs to be found in Table 5.

will be most affected. Therefore the most favourable conditions for testing Bartell's premises are to apply them to atoms in the same environment and neglect H atoms. The amides are a suitable group of compounds to test these ideas. The structures of a large number have been determined with some accuracy, they show considerable variations in bond lengths and bond angles and yet at the same time the environment of the individual atoms tends to be very similar (Table 2). In fact this latter point has always made it difficult to explain the variations in bond lengths: If in these ideal circumstances, there is considerable deviation from the predicted results then the validity of the steric repulsion theory must be doubted.

The data for all those amides, ureas and related compounds have been considered whose structures have been determined by micro-wave spectroscopy or full 3-dimensional X-ray crystallography. A few amides were excluded on the grounds that only 2-dimensional X-ray data had been used in the structure determination and thus was insufficiently reliable.

The "hard sphere" radii used for the atoms C, N, O and S were 1·26 Å, 1·14 Å, 1·13 Å and 1·52 Å. These are the values assigned by Bartell except that the value for C has been modified slightly from 1·25 Å to 1·26 Å. Using these radii and the measured bond-lengths, theoretical bond angles were calculated for the structures being considered and compared with the measured bond angles.

For example in formamide, considering atoms other than hydrogen



$$\text{N-----O} = r_N + r_O$$
$$= 2{\cdot}27\ \text{Å}$$

Hence θ can be calculated and compared with the measured value of 123·6°.

The calculation has been done in this way to be consistent with Bartell and Bright Wilson and it also makes it easier to compare the results.

The results are shown in Tables 3, 4, and 5. Table 3 includes those structures obtained by microwave spectroscopy or by X-ray diffraction where the standard deviations in bond lengths are better than 0·01 Å and the bond lengths have been corrected for thermal motion. Table 4 consists of structures obtained by X-ray diffraction where the standard deviations in bond lengths are better than 0·01 Å but no correction has been made for thermal motion. Table 5 consists of structures obtained by X-ray diffraction where the standard deviation is between 0·01–0·02 Å and there has been no correction for thermal motion. Structures of less accuracy have not been considered.

In Table 3 the standard deviation in the measured bond angles is of the order of 0·5°. In Table 4 the standard deviation claimed is about 0·5° but since no correction has been made for thermal motion the probable error could be at least 1°. In Table 5 the errors will be about 2°.

Comparison of the observed and theoretical bond angles shows that they agree well within the expected limits of error. An impressive feature is that where more than one determination has been made of a structure; the more accurate the determination, the better the agreement between observed and theoretical bond angles.

TABLE 3. COMPARISON OF OBSERVED AND THEORETICAL BOND ANGLES (in degrees)

Molecule	Angle	Obs.	Calc.	Δ
Formamide[a]	NCO	123·6	122·7	0·9
Ammonium Oxamate[b]	NCO	123·8	123·9	0·1
	CCN	115·7	115·9	0·2
	CCO	120·5	120·2	0·3
Sorbamide[c]	NCO	121·7	121·3	0·4
	CCN	115·9	116·5	0·6
	CCO	122·4	121·3	1·1
Thioacetamide[d]	NCS	121·6	121·8	0·2
	CCN	117·7	116·7	1·0
	CCS	120·7	120·0	0·7
Urea[e]	NCO	120·5	119·2	1·3
Thiourea[f]	NCS	120·5	120·2	0·3
Triuret[g]	NCO	125·1	123·7	1·4
	NCO	123·2	123·0	0·2
Mono-fluoroacetamide[h]	NCO	124·0	123·8	0·2
	CCN	118·7	114·4	4·3
	CCO	117·3	117·7	0·4
Ethyl carbamate[i]	NCO	122·4*	123·8	1·4
		124·9†	124·9	0·0
Picolanamide[j]	NCO	125·0	124·0	1·0
	CCN	115·5	114·9	0·6
	CCO	119·5	119·9	0·4
Root-Mean-Square‡				0·75

* Measured at 25°. † Measured at −105°. ‡ Omitting CCN for mono- fluoroacetamide.

[a] R. J. Kurland and E. B. Wilson, *J. Chem. Phys.* **27**, 585 (1957).

[b] B. Beagley and R. W. H. Small, *Proc. Roy. Soc.* (A) **275**, 469 (1963).

[c] S. E. Filippakis, L. Leiserwitz and G. M. J. Schmidt, *J. Chem. Soc.* (*B*) 297 (1967).

[d] M. R. Truter, *Ibid.* 997 (1960).

[e] A. Caron and J. Donohue, *Acta Cryst* **17**, 544 (1964).

[f] M. R. Truter, *Ibid.* **22**, 556 (1967).

[g] H. Ringertz, *Ibid.* **20**, 932 (1966).

[h] D. O. Hughes and R. W. H. Small, *Ibid.* **15**, 933 (1962).

[i] B. H. Bracher and R. W. H. Small, *Ibid.* **23**, 410 (1967).

[j] T. Takano, Y. Sasado and M. Kakudo, *Ibid.* **21**, 514 (1966).

This is well illustrated by the structure determinations on formamide and hydroxyurea.

One obvious exception exists and that is the NCC angle in monofluoracetamide. This molecule is unusual for an amide because normally when there is only one substituent other than hydrogen on the α-C atom it tends to adopt the *cis* rather than the *trans* configuration to the $C{=}O$ bond.[20] However in monofluoroacetamide the C—F bond is *cis* to the C—N bond and the FCCNO framework is essentially planar. An electronegative fluorine atom, close (2·28 Å) to the amide group would obviously introduce additional repulsive forces which are not taken into account in a simple

TABLE 4. COMPARISON OF OBSERVED AND THEORETICAL BOND ANGLES (in degrees)

Molecule	Angle	Obs.	Calc.	Δ
Oxamide[a]	NCO	125·7	125·1	0·6
	CCN	114·8	114·1	0·7
	CCO	119·7	117·8	1·9
Succinamide[b]	NCO	122·0	123·9	1·9
	CCN	115·6	114·9	0·7
	CCO	122·4	120·4	2·0
Hydroxyurea[c]	NCO	122·9	122·5	0·4
Di-fluoroacetamide[d]	NCO	129·3	129·7	0·4
	CCN	114·1	113·3	0·8
	CCO	116·5	116·4	0·1
Root-mean-square				1·2

[a] E. M. Ayerst and J. R. C. Duke, *Acta Cryst.* 7, 588 (1954).
[b] D. R. Davies and R. A. Pasternak, *Ibid.* 9, 334 (1956).
[c] Helen Berman and S. H. Kim, *Ibid.* 23, 180 (1967).
[d] D. O. Hughes and R. W. H. Small, To be published.

"hard sphere" model. These additional repulsive forces would tend to push the amide group away and widen the NCC angle. In difluoroacetamide the two fluorine atoms are approximately symmetrical with respect to the oxygen and nitrogen atoms and consequently any additional repulsive forces should cancel out and a "hard sphere" model should give an accurate picture of the structure. The results obtained confirm exactly these expectations.

The evidence therefore appears to substantiate Bartell's claims that non-bonded interactions are of prime importance in determining molecular geometry. It should be stressed however that even if non-bonded interactions are largely responsible for fixing molecular geometry, it does not mean that conjugation or hyperconjugation are not present. These effects may well be present but they cannot be deduced from bond lengths until the effects of non-bonded repulsions have first been considered. Thus because a C—C bond is 1·54 Å long it does not mean it cannot have some multiple bond character and conversely if a C—C bond is shorter than 1·54 Å it does not necessarily mean it is not a pure single bond.

The implications of this are widespread. Many ideas concerning hyperconjugation, $p\pi$–$p\pi$ and $p\pi$–$d\pi$ bonding, etc. depend on the assumption that a decrease in bond length must mean an increase in double bond character. If non-bonded interactions are important such evidence alone is insufficient and additional support must be forthcoming from other sources.

CONCLUSION

Examination of the structures of amides indicates that non-bonded interactions are of prime importance in determining molecular geometry and the influence of hybridization, conjugation or hyperconjugation would appear to be small. Con-

TABLE 5. COMPARISON OF OBSERVED AND THEORETICAL BOND ANGLES
(in degrees)

Molecule	Angle	Obs.	Calc.	Δ
Formamide[a]	NCO	121·5	125·3	3·8
Acetamide[b]	NCO	123·6	122·1	1·5
	CCN	115·7	115·3	0·4
	CCO	120·7	119·4	1·3
Glutaramide[c]	NCO	122·0	124·9	2·9
	CCN	117·0	114·0	3·0
	CCO	121·0	121·1	0·1
Suberamide[d]	NCO	123·0	124·1	1·1
	CCN	116·5	114·9	1·6
	CCO	120·5	119·0	1·5
Adipamide[e]	NCO	123·0	124·9	1·9
	CCN	115·0	116·5	1·5
	CCO	121·0	122·7	1·7
m-Hydroxybenzamide[f]	NCO	124·4	125·9	1·5
	CCN	116·6	117·6	1·0
	CCO	119·0	120·6	1·6
Nicotinamide[g]	NCO	125·0	124·9	0·1
	CCN	117·0	114·0	3·0
	CCO	118·0	121·1	3·1
Hydroxyurea[h]	NCO	123·9	122·4	1·5
Benzamide[i]	NCO	124·3	124·0	0·3
	CCN	115·6	113·9	1·7
	CCO	120·3	118·9	1·4
6-Amido-3-pyridazone[j]	NCO	123·0	123·2	0·2
	CCN	118·0	118·6	0·6
	CCO	119·0	123·6	4·6
Root-Mean-Square				2·0

[a] J. Ladell and B. Post, *Acta Cryst.* **7**, 559 (1954).
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versely the degree of conjugation or hyperconjugation cannot be deduced from bond lengths and any theory relying on such a deduction must be treated with suspicion.

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