[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 509]

The Dependence of Interatomic Distance on Single Bond–Double Bond Resonance[1]

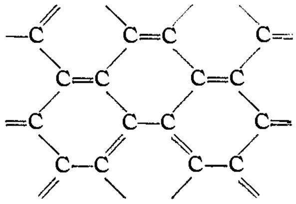
BY LINUS PAULING, L. O. BROCKWAY AND J. Y. BEACH

Introduction

Three years ago it was pointed out[2] that observed values of interatomic distances provide useful information regarding the electronic structures of molecules, and especially regarding resonance between two or more valence bond structures. On the basis of the available information it was concluded that resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.[3] For example, in benzene each carbon–carbon bond resonates about equally between a single bond and a double bond (as given by the two Kekulé structures); the observed carbon–carbon distance, 1.39 Å., is much closer to the carbon–carbon double bond distance, 1.38 Å., than to the single bond distance, 1.54 Å.

In benzene the two Kekulé structures contribute equally. In general, however, the coefficients of the functions corresponding to different structures in the approximate wave function of a molecule may have arbitrary values, and a bond between two atoms may have any intermediate character between the extremes of a pure single bond and a pure double bond. For a series of bonds covering the range between a pure single bond and a pure double bond we expect the interatomic distance to change continuously from the single bond value to the double bond value. In this paper we present evidence regarding the nature of the function expressing the dependence of interatomic distance on single bond–double bond resonance, and then make use of the function in order to obtain information regarding the electronic structures of resonating molecules for which experimental interatomic distance values are available. The effect of resonance on bond angles is also discussed.

The Interatomic Distance Function for Single Bond–Double Bond Resonance.—The carbon–carbon single bond distance is 1.54 Å. (diamond, aliphatic compounds). For the carbon–carbon double bond distance we shall use the value 1.38 Å. given by the table of covalent radii;[4] some support for this is given by Badger's value[5] 1.37 Å. for ethylene. These give the two extreme points of the interatomic distance function for single bond–double bond resonance. The midway point, for fifty per cent. double bond character, is provided by the value 1.39 Å. for benzene;[6] the electronic structure of benzene is represented in the main by resonance between the two Kekulé structures (the contribution of excited structures being small[7]), and this makes each bond resonate equally between a double and a single bond. Another point on the curve is provided by graphite (C–C = 1.42 Å.), in which each bond has one-third double bond character, corresponding to resonance among many structures such as



Through these four points we draw a smooth curve, as shown in Fig. 1, which we accept as representing the dependence of carbon–carbon interatomic distance on double-bond character for single bond–double bond resonance. We believe that by a suitable translation and a change of vertical scale (to give the correct end-points) the same function can be used for bonds between other atoms, and probably also for double bond–triple bond resonance. This use of the curve will be illustrated below.

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(1) Part of the material in this paper was presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(3) The following argument, suggested by Professor P. M. Morse, shows that this conclusion is reasonable. Of two potential functions corresponding to two structures, the one with the smaller value of the equilibrium internuclear distance will have the greater curvature in the neighborhood of the minimum [see for example, R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934)]. Hence the more stable of the two resultant potential functions corresponding to resonance between these two structures will tend to have its minimum in the position determined by the original curve of greater curvature, that is, near the smaller value of the internuclear distance.

(4) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(5) R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

(6) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(7) A possibly more accurate value for the double bond character of the bonds in benzene (0.46) is obtained by considering all five canonical structures with weights equal to the squares of their coefficients in the wave function. There is some uncertainty as to the significance of this, however, because of the non-orthogonality of the wave functions for the canonical structures, and for chemical purposes it is sufficiently accurate to follow the simple procedure adopted above.

It is seen that a small amount of double bond character causes a large decrease in interatomic distance below the single bond value, whereas only a small change from the double bond value is caused by even as much as fifty per cent. single bond character.[8] In consequence, the interatomic distance criterion for resonance provides quantitative information only through about one-half of the bond character region.

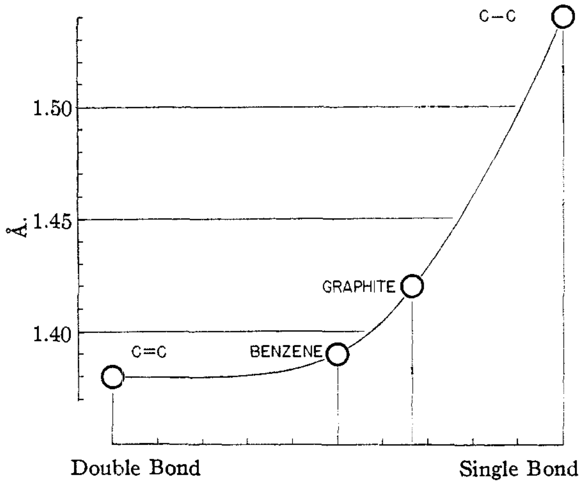

Fig. 1.—The empirical function expressing the dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance.

The applicability of the curve to bonds other than carbon–carbon can be tested with the data for carbon–oxygen and nitrogen–oxygen bonds given in Table I, the predicted distances being obtained from the table of covalent radii for pure single and double bonds, and from the curve (with end-points determined by the table) for bonds of intermediate type. The carbonate and nitrate ions resemble graphite in that the double bond resonates among three positions, whereas in the carboxyl and nitro groups, as in benzene, the double bond resonates between two positions. It is seen that there is approximate agreement between predicted and observed values.

TABLE I

COMPARISON OF PREDICTED AND OBSERVED INTERATOMIC DISTANCES

Amount of double bond character	Predicted distance	Observed distance
	Carbon–Oxygen Bonds	
0	1.43 Å.	1.42 Å. in $(CH_3)_2O$[a] 1.44 in CH_3ONH_2[a]
$^1/_3$	1.32	1.31 (1.26) in $(CO_3)^{=}$[b]
$^1/_2$	1.29	1.29 in $(HCOOH)_2$[c]
1	1.28	
	Nitrogen–Oxygen Bonds	
0	1.36 Å.	1.37 Å. in CH_3ONH_2[a]
$^1/_3$	1.26	1.22 (1.26) in $(NO_3)^-$[b]
$^1/_2$	1.23	1.21 in CH_3NO_2[a]
1	1.22	

[a] Preceding papers. [b] Preliminary values obtained through redetermination of parameters in crystals (calcite and sodium nitrate) by Mr. Norman Elliot. The values in parentheses are based on older parameter determinations. [c] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934). The value 1.25 Å. reported in crystals of oxalic acids and oxalates is probably less reliable.

The Use of the Interatomic Distance Function in Discussing the Electronic Structure of Molecules.—The observed interatomic distances listed in Table II are interpreted with the aid of the curve of Fig. 1 to lead to the assignment of fractional double bond character as given in the last column. It is seen that a single bond between conjugated double bonds (cyclopentadiene) or conjugated benzene rings (biphenyl) *p*-diphenylbenzene, has about 15 or 20% double bond character,[9] whereas a single bond between conjugated

TABLE II

INTERATOMIC DISTANCES AND BOND TYPE

Molecule	Bond	Observed distance	Amount of double bond character
Cyclopentadiene	C—C	1.46 Å.[a]	0.20
p-Diphenylbenzene	C—C	1.48[b]	.14
Biphenyl	C—C	1.48[c]	.14
Cyanogen	C—C	1.43[d]	.29
Diacetylene	C—C	1.43[d]	.29
Urea	C—N	1.37[e]	.28
Thiourea	C—N	1.37[f]	.28
Cyanuric triazide	C—N	1.38[g]	.25
Carbon suboxide	C═C	1.30[h]	.20[i]
	C═O	1.20[h]	.20[i]

[a] Preliminary result of electron diffraction study in this Laboratory. [b] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933). [c] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932). [d] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933). [e] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934). [f] R. W. G. Wyckoff and R. B. Corey, *ibid.*, **81**, 386 (1932). [g] I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935). [h] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933). [i] Triple-bond character.

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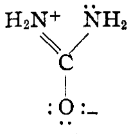
(8) Verification of the shape of the curve has been obtained with the collaboration of Dr. J. Sherman by the theoretical treatment of a somewhat similar problem (the effect of *s-p* hybridization of bond orbitals on interatomic distance).

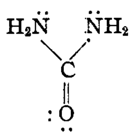
(9) The comparison of these results with the simple theory of conjugated systems [Pauling and Sherman, *J. Chem. Phys.*, 1, 679 (1933)] is not straightforward because of non-orthogonality of the canonical structures. If we assume that the double bond character is given by the square of the coefficient of the structure $\overline{-\;=\;-}$ in the normalized wave function for a system of two conjugated double bonds the simple theory leads to the value 0.25 in approximate agreement with the experimental result.

triple bonds (cyanogen, diacetylene) has about 30% double bond character. In cyanuric triazide the reported distance for the bond linking an azide group to the cyanuric ring corresponds to about 25% double bond character.

In urea and thiourea the ionic structures such as



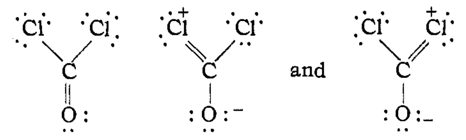
are of sufficient importance to give each C–N bond about 28% double bond character. In case these structures were equivalent to the structure



giving complete resonance, each bond would have one-third double bond character, as in the carbonate, nitrate, and guanidonium ions. The experimental result shows that resonance is nearly complete.

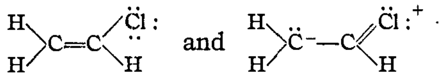
In carbon suboxide, for which the structure $:\ddot{O}=C=C=C=\ddot{O}:$ is most important, structures such as $^-:\ddot{O}-C\equiv C-C\equiv O:^+$ contribute about 20% triple bond character to each bond.

Resonance of a Carbon–Chlorine Bond and an Adjacent Double Bond.—We expect the phosgene molecule to resonate among the structures



of which the first is the most important, the second and third making only small contributions to the normal state of the molecule. The value 1.68 ± 0.02 Å. for the C–Cl distance, reported in the preceding paper,[10] corresponds to 17% double bond character for the carbon–chlorine bonds, calculated with the curve of Fig. 1, with end points C–Cl = 1.76 Å. and C=Cl = 1.58 Å. The value C–Cl = 1.70 ± 0.02 Å. in thiophosgene leads to 12% double bond character, indicating that the ionic structures make a smaller contribution for this molecule than for phosgene.

We might predict that of the six chloroethylenes the C–Cl distance would be smallest in vinyl chloride, which resonates between the structures



and largest in tetrachloroethylene, in which the effect of the double bond is divided among four carbon–chlorine bonds. This is found experimentally (Table III), except that the distance reported for *cis*-dichloroethylene is about 0.02 Å. smaller and that for vinyl chloride somewhat larger than expected. The amounts of double bond character shown in the table are reasonable—about 15% for mono- and dichloroethylenes, 10% for trichloroethylene, and 6% for tetrachloroethylene.

TABLE III

INTERATOMIC DISTANCES AND BOND TYPE FOR CARBON-CHLORINE BONDS

Molecule	C-Cl distance	Double bond character
Phosgene	1.68 ± 0.02 Å.	0.17
Thiophosgene	1.70 ± .02	.12
CH_2CHCl	1.69 ± .02	.14
CH_2CCl_2	1.69 ± .02	.14
cis-CHClCHCl	1.67 ± .03	.20
trans-CHClCHCl	1.69 ± .02	.14
$CHClCCl_2$	1.71 ± .03	.10
C_2Cl_4	1.73 ± .02	.06

The effect of this partial double bond character on the chemical properties of chlorine atoms conjugated to double bonds is well known; it corresponds in the main to a diminution in reactivity. The correlation with bond angles is discussed in a later section of this paper.

Inasmuch as the conjugation properties of a double bond and a benzene ring are closely similar,[11] we expect for the halogen substituted benzenes interatomic distances similar to those for the halogen ethylenes. De Laszlo[12] has reported the values C–Cl = 1.69 Å., C–Br = 1.88 Å., and C–I = 2.05 Å., corresponding to 14, 6, and 10% double bond character, respectively.[13]

The Dependence of Bond Angles on Single Bond–Double Bond Resonance.—In a molecule such as phosgene or 1,1-dichloroethylene the value 125°16′ for the angle Cl–C–O (β) is predicted by the theory of the tetrahedral carbon atom in case that the C–Cl bonds have no double bond character. If the double bond resonates equally among all three positions, giving the Cl–C bond one-third double bond character, we expect from symmetry

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[10] Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 1935).

[11] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933).

[12] H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 690 (1934).

[13] The interatomic distance values given are stated to hold for hexahalogen, *sym*-trihalogen and *p*-dihalogen benzenes. We expect the distances in these different compounds to be different, however; and investigation of these and other halogen compounds is under way in this Laboratory. De Laszlo has also reported values of C–Br and C–I distances in ethylenic and acetylenic compounds in a letter to *Nature*, **135**, 474 (1935).

the value 120° for β. Between these limits the dependence of β on the amount of double bond character of the C–Cl bonds may be postulated to be given by a curve similar in shape to the interatomic distance curve of Fig. 1. If this is so, there would be a linear relation connecting the angle β and the C–Cl distance, between the points β = 125°16′, C–Cl = 1.76 Å. and β = 120°, C–Cl = 1.64 Å. (as given by the curve for one-third double bond character). From a similar discussion, the other chloroethylenes (except vinyl chloride) would be expected to fall roughly on the same line.

A test of this relation is shown in Fig. 2, the seven points being those determined experimentally for phosgene and the six chloroethylenes.

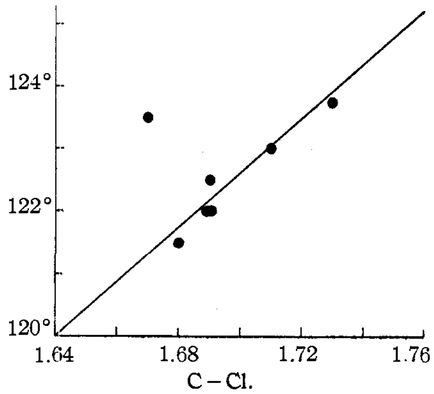
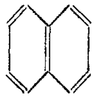
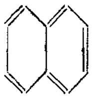
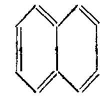
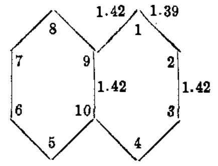


Fig. 2.—The relation between bond angle and carbon-chlorine distance for phosgene and the chloroethylenes.

It is seen that, with one exception, the points lie very close to the straight line drawn according to our assumptions, the displacements being much less than the probable errors of the experimental values. The exceptional point is that for *cis*-dichloroethylene, the discrepancy confirms the suggestion made in the preceding section that our results for this substance are slightly in error.[14] It is surprising that vinyl chloride obeys the same relation, as there is no apparent reason for the angle to be much different from 125°16′.

Interatomic Distances in Polynuclear Aromatic Hydrocarbons.—As a further example of the use of the interatomic distance function we shall discuss the polynuclear aromatic hydrocarbons.

For naphthalene there are three unexcited structures   and  Giving these equal weights, we obtain the result that the 1–2 bonds have $^2/_3$ double bond character and all others $^1/_3$. These correspond to the values 1.39 Å. for the 1–2 interatomic distances (including 3–4, 5–6 and 7–8), and 1.42 Å. for all others, giving the configuration



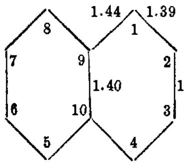
A possibly more reliable prediction can be made on the basis of Sherman's wave function for naphthalene,[15] by considering all 42 canonical structures. The fractional double bond character of a bond can be considered to be given approximately (neglecting non-orthogonality of the canonical wave functions) by the expression

$$\sum_i' a_i^2 / \sum_i a_i^2$$

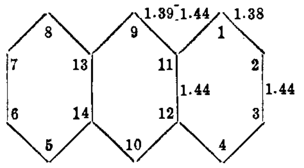
in which a_i represents the coefficient for the ith structure; the unprimed sum includes all structures of the set of 42, and the primed sum those for which the bond in question is a double bond. The results of this calculation are the following:[16]

Bond	1–2	2–3	9–1	9–10
Double bond character	0.60	0.33	0.26	0.43
C–C distance	1.39 Å.	1.42 Å.	1.44 Å.	1.40 Å.

corresponding to the configuration



The four unexcited structures for anthracene, given equal weights, lead to $^3/_4$ double bond character for the 1–2 bonds, $^1/_2$ for the 9–11 bonds and $^1/_4$ for others, the predicted configuration being



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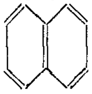
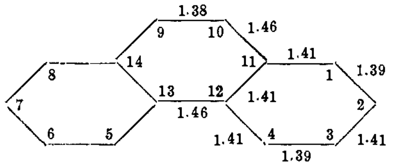
[14] The discrepancies are removed by increasing the C–Cl distance by 0.02 Å., to 1.69 Å., and decreasing the angle by 1°, to 122°30′. These changes are within the estimated probable errors of our determination, ±0.03 Å. and ±1°, respectively.

[15] J. Sherman, *J. Chem. Phys.*, **2**, 488 (1934).

[16] It may be pointed out that the changes from the simple calculation given above result mainly from the fact that the coefficient for the structure  is larger than that for the other unexcited structures.

For phenanthrene the five unexcited structures lead to $^4/_5$ double bond character for the 9–10 bonds, $^3/_5$ for the 1–2 bonds, $^2/_5$ for the 1–11, 11–12 and 4–12 bonds, and $^1/_5$ for the 10–11 and 12–13 bonds, and the predicted configuration is



Similar prediction can be made for larger molecules. It must be pointed out that the contributions of excited structures become important for bonds with small double bond character, inasmuch as in conjugated systems excited structures alone may lead to as much as 20% double bond character; it is probable that the maximum carbon–carbon bond distance in aromatic hydrocarbons is about 1.46 Å., the minimum being the double bond distance 1.38 Å.

The predicted average interatomic distance is 1.41 Å. in naphthalene, anthracene and phenanthrene, this value being somewhat larger than the benzene value (1.39 Å.). With increase in size of the hydrocarbon the carbon–carbon distances should all approach the graphite value 1.42 Å.

The only experimental values of sufficient accuracy to permit a test of the predicted values are those obtained by Robertson in his careful and thorough x-ray investigations of the structure of crystals of naphthalene[17] and anthracene.[18] In each of these molecules Robertson reports the value 1.41 Å. for the average carbon–carbon bond distance, in complete agreement with the predicted value.[19] He does not discuss individual variations from the average; however, measurements made on his reproduced electron distribution projections (Fig. 2 for naphthalene, Fig. 2 for anthracene) show differences of 2 or 3% in the predicted directions.[20]

Summary

Using experimental values for carbon–carbon bonds, a function is plotted showing the dependence of interatomic distance on bond character for single bond–double bond resonance. This function is tested with data for other bonds, and used in the discussion of the electronic structure of molecules containing conjugated double or triple bonds or aromatic nuclei and of molecules containing carbon–chlorine bonds adjacent to double bonds. The dependence of bond angles on single bond–double bond resonance is discussed. Values of carbon–carbon bond distances in polynuclear aromatic hydrocarbons are predicted and compared with the existent experimental data.

[17] J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 674 (1933).

[18] J. M. Robertson, *ibid.*, **A140**, 79 (1933).

[19] The data for chrysene [J. Iball, *ibid.*, **A146**, 140 (1934)] are also compatible with this value.

[20] The value 1.41 Å. has also been reported for the carbon–carbon distance in benzene derivatives. We think it probable that this is 0.02 Å. too large.

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[CONTRIBUTION FROM THE ONTARIO RESEARCH FOUNDATION]

Vapor Pressures of Certain Glycols

BY O. J. SCHIERHOLTZ AND M. L. STAPLES

In connection with other current research work, the authors have had occasion to determine the vapor pressure curves for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene.

A search of the literature for physical constants of these compounds revealed the fact that comparatively little has been published. With the exception of ethylene glycol, no vapor pressure data could be found, and many of the physical constants which are recorded are not at all concordant. The densities and refractive indices have been determined for all the above glycols, and are tabulated below.

All the compounds used in the determinations were purified by distillation, suitable neutralizing agents being used to obtain completely neutral, colorless, odorless products. The purities were such that the refractive index of successive fractions did not differ by more than 0.00038, and in most cases the difference was considerably less.

The starting materials for those glycols not synthesized in this laboratory were as follows: ethylene glycol and 1,2-propylene glycol, Carbide