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DISCUSSION

Robert S. Mulliken

*General Discussion of Questions raised in the Contributed Papers**

I SHOULD like to make several specific comments in reaction to some of the very interesting articles in this Paper Symposium. Basically, I am in agreement with Bright Wilson's agnostic views about why bond lengths are as they are. I believe that there are a number of big and little reasons which contribute, varying in importance from case to case. This makes it difficult to pick out and assign correct weighing to the real reasons, either in general or in particular cases.

The greatest difficulty of all may be that it is almost impossible for any one individual to collect and to keep in view all at once the now extremely large and very varied mass of both experimental and theoretical evidence, all of which must be most cautiously and critically and simultaneously evaluated if he is to reach sensible conclusions. The whole field is so extensive and so complex, and experiment and theory are so intimately interwoven, that it is easy to overlook or underemphasize relevant considerations, and extremely difficult to obtain and maintain a well-balanced judgment containing a correct proportion of open-minded tentativeness. Perhaps for the moment we should relax a bit. It seems likely that, before long, new experimental data and new theoretical calculations of much increased accuracy will help us to see things more clearly.

Nevertheless, while I am open-minded about new evidence, both experimental and theoretical, I hold rather strongly to the views I have expressed in two recent articles in *Tetrahedron*.[1,2] These papers were written in some haste and are not quite as clearly stated as one might wish. Hence I should like here, along with other comments, to reiterate and try to clarify some of the main points made there.

(1) I should like to emphasize the importance of a due regard for the hierarchies of conjugation and hyperconjugation types, as deduced from either valence-bond or molecular orbital theory, and supported by experimental evidence.[1] Namely, isovalent conjugation should give the largest effects, sacrificial conjugation less, and the same with hyperconjugation. Conjugation effects in any given category should be larger than hyperconjugation effects. Further, we should distinguish homodative, (more or less) non-dative, and dative conjugation or hyperconjugation as effects of diminishing importance in that order.

(2) Lide's paper[3] emphasizes clear evidence for rather large bond length shortenings attributable to dative isovalent conjugation, which means partial electron donation from a π lone pair of a donor group into an unsaturated system. This donor-acceptor action is increvalent from the point of view of the donor group (one new π bond is

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* This work was assisted by the Office of Naval Research.

[1] R. S. Mulliken, *Tetrahedron* 5, 253 (1959).

[2] R. S. Mulliken, *Tetrahedron* 6, 68 (1959).

[3] D. R. Lide, Jr., This Symposium, p. 125.

formed) but sacrificial from that of the unsaturated system (one carbon atom gets de-bonded); *over-all* it is isovalent.

(3) On the other hand, Lide, in agreement with others, points out clearly that in hydrocarbons, C–C bond lengths can be predicted in most cases within experimental error by assuming a fixed covalent single-bond radius for what are usually considered to be sp, sp^2 and sp^3 carbon atoms. In other words, one has indeed a rather reliable and very *simple recipe* for predicting C–C bond lengths in hydrocarbons if one thinks only in terms of hybrid types without considering π-electron delocalization. So far, so good.

But in terms of fundamental understanding, and of the interpretation and prediction of other properties than bond lengths, an open-minded consideration of all the evidence, experimental and theoretical together,[1,2] leaves little doubt that π electron delocalization makes substantial contributions to observed C–C bond shortenings in conjugated and hyperconjugated systems. My best present judgment is that on the whole hybridization contributes somewhat more than electron delocalization to the observed shortenings, but that the two causes are of the same order of magnitude; and that in addition, other causes make contributions which usually are smaller, but sometimes may be fairly important.

An important reason why it is difficult to decide experimentally between hybridization and electron delocalization as causes of bond shortening is the fact that the two effects largely operate in parallel: wherever there is double-bond conjugation, there is a change in hybridization, and when there is triple-bond or cumulene-type conjugation, there is a further change. Under these circumstances, it becomes rather necessary, and proper, to place considerable reliance on theory, provided it is reliable theory. As to the reliability of the theory now being used, this seems rather well buttressed,[2] although there are questions of detail, and perhaps *small* doubts about some major points, so that one must not be too dogmatic. In any event, it is the same delocalization theory that seems clearly *necessary* to explain the observed bond shortenings in dative isovalent conjugation which is used in estimating the effects of electron delocalization in conjugation and hyperconjugation in general.

(4) I am inclined to agree with Dewar that the term conjugation (now extended to include isovalent conjugation, as in benzene) can best be used to denote comprehensively the alterations in chemical and physical characteristics which are found *empirically* in molecules when single bonds are located between double or triple bonds or between the latter and lone-pair donor groups, and so on.[2] Such a phenomenological definition and concept of conjugation seems to be safer and historically better justified than one based on theoretical explanations of the *reasons* for the empirical differences between conjugated and unconjugated systems. Thus, for example, bond shortenings of C–C bonds, *whatever* the cause or causes, may be accepted as characteristic manifestations of conjugation. In such a definition, primary emphasis must, however, be placed on *ground state* behavior, since excited electronic states are many and varied in nature.

Having gone so far, it should nevertheless be noticed that even the most completely empirical definition and concept of conjugation still indispensably involves a definitely theoretical concept, namely that of chemical bonds. The above-discussed supposedly empirical definition of conjugation can be stated only in terms of what happens when various juxtapositions of bonds are present in a molecule, and the existence of bonds, whether classically or quantum-mechanically conceived, is a theoretical concept. Dewar's concept of conjugation is then apparently no more than *semi-empirical.*

Very similar comments are applicable to the concept of hyperconjugation. Although historically this concept was introduced in a context of theoretical explanation with emphasis on electron delocalization, it would seem to be sounder to use the term to denote the very real changes in chemical and physical properties which are observed to be associated with the presence of methyl or substituted methyl or methylene groups close to π bonds in unsaturated systems. However, I am not at all convinced that it is necessary to abandon the term "hyperconjugation" in favor of a new term "semiconjugation", as Dewar and Schmeising have recently proposed,[4] merely because the introduction of "hyperconjugation" was accompanied by explanations in terms of electron delocalization.

The foregoing comments and proposals, made in the interest of clarity of definition, of course do not involve any modification of beliefs as expressed in item (3).

Concerning the subclassification of conjugation and hyperconjugation into isovalent and sacrificial, and dative, homodative and non-dative categories as mentioned in item (1), it may be objected that the adjectives thus introduced are based on theory, and thus are inconsistent with the proposal to regard conjugation and hyperconjugation as semi-empirical concepts. This objection may be countered as follows. (a) I believe that an examination of the empirical properties of each of the sub-classes of molecules distinguished by the various adjectives will show distinctive features, blurred or even concealed, to be sure, by extraneous factors in the case of the weaker types of conjugation and especially hyperconjugation. (b) Granting that there are empirically distinct sub-classes, names are needed to distinguish them. The names adopted have, to be sure, a theoretical origin, but the theory involved goes beyond classical bond theory (which had to be assumed in setting up a semi-empirical concept of conjugation or hyperconjugation) only by making use of the simplest possible, and (in the case of conjugation, at least) generally accepted classically-bonded resonance structures. The main point is that some sort of terminology is needed, and the use of designations based on the theory of resonance between classical bond structures supplies this need in a way which is especially convenient and self-explanatory even if one does not wish to accept all its implications literally. However, I myself see no need to reject at least partial validity of the theoretical implications of the proposed terminology. It is very useful to distinguish sacrificial from isovalent conjugation, and to distinguish dative from other kinds of conjugation. I have found these distinctions most helpful in obtaining better insight into the structures of molecules. An interesting example is a comparison between aniline or phenol; with dative isovalent conjugation, nitrobenzene, with dative sacrificial conjugation, and *p*-nitroaniline, where again there is dative isovalent conjugation.[1] That nitrobenzene is in a different class from the others seems not to be generally realized.

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[4] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 11, 96 (1960). I disagree or have very strong reservations on the main conclusions in that paper, but because of pressure of other work must postpone detailed comments. However, I should like to express sincere regret if I have misinterpreted or misquoted their earlier paper (*cf.* footnotes on p. 97 and p. 101 of their 1960 paper). In explanation, I should like to mention that at the time my paper was written, I had not seen the manuscript of their paper, but was relying on notes I had made based on Professor Dewar's oral presentation and discussion at the 1958 Conference on Hyperconjugation, possibly a subjective element may have somewhat colored these notes.

(5) Much confusion in the literature has, I believe, been generated by the identification of the concept of hyperconjugation with the Baker-Nathan effect.[1] Experimentally they are different concepts, while in terms of the π delocalization theory of hyperconjugation, the Baker-Nathan effect is *not* hyperconjugation, but may be attributable to *differences* between C—C and C—H hyperconjugation, although other causes may be partly or largely responsible. The delocalization theory sees no difference in kind between C—C and C—H hyperconjugation, but admits the possibility of quantitative differences, experimental evidence on which has been elucidated especially by Taft and co-workers.

Historically, the π delocalization theory of what would now be called isovalent hyperconjugation was apparently first used in a 1933 paper of mine on twisted ethylene, while the applicability of the same theory to examples of what would now be called sacrificial hyperconjugation was early recognized by Wheland, and by Hückel. The same idea was also stated briefly in the original paper of Baker and Nathan, but in later papers they restricted the idea to what is now called C H hyperconjugation, and (perhaps at first tentatively) *assumed* C—C hyperconjugation to be non-existent. Thereby the experimentally observed *differences* between C—C and C—H sacrificial hyperconjugation—the Baker-Nathan effect—became identified with the later-proposed term hyperconjugation. Here it may be recalled that sacrificial hyperconjugation is expected to be a relatively weak effect, so that differences between C-H and C—C sacrificial hyperconjugation should thus be still weaker and easily masked (or simulated) by other effects, for example by solvent effects (Schubert, Shiner). In any event, the delocalization theory of hyperconjugation does not see any uniqueness in H atoms as carriers of hyperconjugation, and the experimental evidence of Taft and others seems to bear out this theoretical expectation.

In their original paper, Baker and Nathan referred to their effect as a "new mechanism of electron release"; electron release was considered an important characteristic and criterion of the effect. However, electron release is not an essential or important feature of the delocalization theory of ordinary (sacrificial) hyperconjugation or conjugation; in this respect it is entirely different from dative hyperconjugation or conjugation, where electron release *is* an essential intrinsic characteristic and criterion. The occurrence of a moderate amount of electron release from a CH_3 group to an unsaturated group in ordinary hyperconjugation is attributable to a somewhat greater electronegativity of the latter than the former. For example in propylene it would correspond to a mild predominance of the resonance structures $H_3{}^{+}{\equiv}C{-}CH{-}\bar{C}H_2$ and $H_3{}^{+}{=}C{=}CH{-}\bar{C}H_2$ over $H_3{}^{-}{\equiv}C^{+}{-}CH{-}C^{\cdot}H_2$ and $H_3{}^{-}{=}C^{+}{-}C\,H{-}C^{\cdot}H_2$, all these being accompanied by $H_3{\equiv}C{-}CH{-}\dot{C}H_2$ and the predominant structure $H_3{\equiv}C{-}CH{=}CH_2$.[1] On substituting a CMe_3 or a CF_3 group for the CH_3 group, the delocalization theory predicts analogous resonance structures, but in the case of the CF_3 group, electron release would be expected to be predominantly *to* it instead of from it because the quasi-π orbitals of F_3 would be more electronegative than the π orbitals of the double bond, opposite to what seems to be true of the quasi-π orbitals of H_3 in the CH_3 group.

In my opinion, doubts and questions about the cause or causes of the Baker-Nathan effect have no conclusive bearing on the general phenomenon of sacrificial hyperconjugation. On the whole, the Baker Nathan effect, in harmony with other evidence, does seem to support the idea that C—H hyperconjugation is a stronger effect than

C - C hyperconjugation. However, it appears also that the evidence is not very conclusive because of the possibility of other small masking and/or simulating effects.

A further point is that the properties of activated states of hyperconjugated systems, on which according to rate theory the Baker Nathan effect usually or often depends, may not necessarily always parallel those of the ground state, although there is evidence that they usually do. A similar but stronger statement is applicable to conjugated systems.

For electronically excited states of hyperconjugated and conjugated molecules, new considerations enter and can often become important. The properties of electronically excited or ionized states may be expected to differ from state to state and from one type of conjugated or hyperconjugated molecule to another.

(6) The interesting studies of Schubert and collaborators on electronic spectra as presented in this Symposium[5] and in an earlier paper afford a basis for valuable new insight into the theoretical understanding of dative conjugation and hyperconjugation. In agreement with others[6] they interpret the "principal" band spectra of molecules of the type R  —X, where R is an alkyl group and X is either a π donor group or the π acceptor group NO_2, as belonging to the category of what have been called intramolecular charge-transfer spectra. It seems fairly sure that this interpretation of the "principal" spectra is reasonably correct, although a thorough theoretical study will be desirable.

The theory of *intermolecular* charge-transfer or donor-acceptor complexes and their charge-transfer spectra, is directly applicable also to molecules stabilized by dative conjugation or hyperconjugation. In an intermolecular charge transfer complex between a π-electron donor and a π-electron acceptor molecule, the association of the two molecules in their ground states to form a complex is explained by the resonance energy associated with resonance between the predominant no-bond structure and a smaller amount of dative structure. From this there follows also the necessity for a complementary excited "charge-transfer" state in which the dative structure is predominant while the no-bond structure is present to a minor extent. A spectroscopic transition from the ground state to the charge-transfer state corresponds to the charge-transfer band. The delocalization theory of dative conjugation, and of the associated charge-transfer spectra, is identical with that of intermolecular charge-transfer stabilization and spectra of π-π complexes, except that here the donor acceptor action involves two π-electron *groups* already bound together by a σ-bond, instead of two separate π-electron molecules.

In the application of this theory to the molecules R -  --D studied by Schubert and associates, where D is a π-donor group, the following sets of resonance structures I IV are those of most importance or interest, for both the ground state and the charge-transfer state. (The number of resonance structures in each set is given in parenthesis after the formula for a typical member of the set.) The structures are written for the case that R is CH_3, but if R is another alkyl group, it is to be understood

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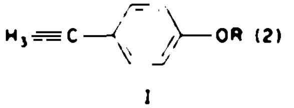
[5] W. M. Schubert, R. B. Murphy and J. Robins, This Symposium, p. 199

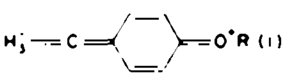
[6] S. Nagakura and J. Tanaka, *J. Chem. Phys.* **22**, 236 (1953); *Ibid.* **23**, 1441 (1955); *Ibid.* **24**, 1274 (1956). S. Nagakura, *Mol. Phys.* **3**, 105 152 (1960). H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* A **68**, 601, 969 (1955)

that C is to be substituted for one or more of the H atoms. Further, for vividness of illustration, D has been taken as an OR group. Besides I-IV, there are also other structures which may be of appreciable importance, especially in the charge-transfer state. There may be considerable admixtures of other excited-benzene-like structures, but probably not enough to alter the conclusions discussed here, but the essential points of interest here can be made by considering structures I-IV only.



I

II



III

IV

In IV, the o indicates an unpaired electron, or also (to a lesser extent) structures with H_3^+ or H_3 and in each case an opposite charge on the ring. The interaction of structures II and I is dative isovalent conjugation, that of III with I is dative isovalent hyperconjugation, while that of IV with I is ordinary sacrificial hyperconjugation as in toluene. In dative conjugation or hyperconjugation, *one-directional* charge transfer is intrinsic. In ordinary sacrificial hyperconjugation or conjugation, charge transfer occurs more or less equally (if at all appreciably) in both directions.

The relative weightings of I-IV in the ground state (N) and in the charge-transfer state (CT) can be estimated *qualitatively* beyond reasonable doubt. For vividness, the following are given as plausible quantitative guesstimates of the fractional amounts of the various structures, with of course no claim to accuracy. Structures I must surely predominate in the ground state, and structures II in the CT state, in agreement with relation (1) as stated in the paper by Schubert and associates. But because the hyperconjugated structure III (an example of Siebold's "anionic hyperconjugation")[6] is hyper-isovalent with II, it can be expected to make a considerable contribution in the CT state, and *certainly* a much larger contribution than in state N. The CT state should therefore be considerably stabilized by structures of type III (and IV) relative to the case where no *p*-alkyl group is present, in which case structure III cannot occur. The ground state, however, should be much less stabilized by these structures.

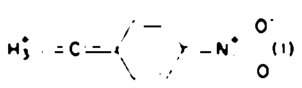
	I	II	III	IV
N	0.87	0.10	0.02	0.01
CT	0.12	0.72	0.12	0.04

The frequency ν_{max} of the absorption band corresponding to the transition from N to CT (Schubert's "principal" band) is therefore expected to be decreased when R is substituted for H, exactly as is found by Schubert and collaborators. Thus the delocalization theory of isovalent hyperconjugation furnishes an entirely reasonable and satisfactory explanation of what is observed. Schubert's further observation that the nature of the alkyl group R makes relatively little difference in the observed shift indicates that dative isovalent hyperconjugation of the kind here involved is, at least for CT excited states, about equally effective whether it be C—H or C—C hyperconjugation. (The observed detailed differences between R groups will not be discussed here.) It does not necessarily follow that the same near-equality must be expected in general. Also, the near-equality here should not be taken as contradicting evidence that C—H hyperconjugation is stronger than C—C hyperconjugation in ground states or in reaction rates.

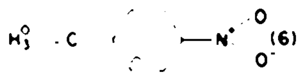
A similar discussion can be given for Schubert's earlier work on the charge-transfer spectra of molecules of the type R  $-NO_2$. Here again we may consider four sets of structures, of types V–VIII,

V

VI



VII



VIII

The interaction of structures VI with V is dative *sacrificial* conjugation, hence should be weaker than that of II with I, where the resonance is isovalent. The interaction of VII with V is dative sacrificial hyperconjugation, that of VIII with V is ordinary sacrificial hyperconjugation as in toluene. The following are guesstimates of the weightings of V–VIII in the N and CT states of the *p*-alkyl nitrobenzenes. In these molecules, structures VIII and VII are *both* hyperisovalent with VI (*all* are sacrificial relative to V), so that the ordinary hyperconjugation structures VIII should be more prominent here than the corresponding structures IV, which are sacrificial relative to I–III for molecules R-  D.

	V	VI	VII	VIII
N	0.95	0.03	0.01	0.01
CT	0.03	0.60	0.15	0.24

Just as in molecules of type R  D, extra structures (here VII and VIII) are introduced by the presence of the *p*-alkyl group, and these must unquestionably be much more important for the CT than for the N state, so that the former should be stabilized more than the latter, and ν_{max} for the CT ← N absorption process should again be decreased, just as has been observed by Schubert and collaborators.

It is seen that the π-electron delocalization theory of hyperconjugation, as approximated here in terms of resonance structures, gives a straightforward and unambiguous explanation of the lowering of the frequency of the charge-transfer band by *p*-alkyl substituents in both donor-group-substituted and acceptor-substituted benzenes.

As has already been stressed in Comment (5), the π-electron delocalization theory of ordinary sacrificial hyperconjugation does not require the methyl or other alkyl group (as e.g. in toluene or t-butylbenzene) to be intrinsically either a quasi-π electron donor or a quasi-π acceptor. *Both* structures should be present in nearly equal but perhaps relatively small amounts (the predominant hyperconjugative structure in that event being the long-bond structure); but the weight of evidence seems to indicate that in ordinary sacrificial hyperconjugation the donor function of the alkyl group (or at least of the methyl group) does predominate somewhat. (At the same time, these groups release electronic charge fairly strongly by the *inductive*, i.e. σ-bond, route.)

Structures III and VII (hyperisovalent respectively with II and VI) show alkyl groups functioning respectively as electron acceptors and as electron donors in *dative*-hyperconjugative resonance structures which must be of appreciable importance in stabilizing charge-transfer states. This amphoteric functioning of the alkyl group, with its charge transfer direction governed by whether the other substituent is a strong electron donor or acceptor, is entirely reasonable and consistent with the theory of sacrificial hyperconjugation according to which in the *absence* of strong direction neither the donor nor the acceptor role is strongly emphasized.

C. A. Coulson

Comments on paper by D. R. Lide

DR. LIDE throws almost all the responsibility for bond length changes in carbon bonds on to changes of hybridization. I believe this to be one of the important factors, but the effect must be more subtle than is sometimes supposed. Thus, changes of hybridization in an isolated carbon atom make no difference whatever to the first-order density matrix. If we make any four orthogonal hybrids out of $sp_xp_yp_z$ the resultant charge-cloud is still spherically symmetrical. Thus hybridization can only achieve its effect in terms of the second-order density matrix, and presumably even here it is largely a question of the difference between the electron correlation terms for electrons with coupled, or with random, spins. When the matter is thought of in terms of the electron density, it is surprising that such characteristic differences are found as is shown by experiment. My own opinion, therefore, is that either we should be content with a very simple type of presumed relation between hybridization and bond length, or we must look for a much more sophisticated analysis, in which even the concept of hybridization may not be adequate.

A situation of the kind just described would not apply to atoms where there is a lone-pair of electrons (e.g. NH_3). For here we have what Moffitt called second-order hybridization, and even the single particle density function is dependent on the hybridization parameters.

C. A. Coulson

Comments on paper by B. P. Stoicheff

ONE of the most disturbing features of this very interesting paper is the observation that although in many cases the electron-diffraction and spectroscopic values agree excellently, yet for CH and CD in CH_4 (and CD_4), they differ by an amount between 0·010 and 0·020 Å. What can be the origin of this difference, which is of the order of magnitude of one-half the classical amplitude of vibration! Further, why is the diffraction value larger than the spectroscopic one, when the following argument would lead us to expect the opposite? The spectroscopic bond length is based on moments of inertia, and therefore is determined almost entirely by the nuclei. We may say that this gives a very reliable length (suitably averaged, of course!) for the internuclear distance. The electron diffraction value involves both nucleus and charge-cloud. So far as the nucleus is concerned, the agreement with spectroscopic measurements should ideally be almost perfect. But so far as the charge-cloud is concerned, we should expect small differences depending on the lack of spherical symmetry in the electron density around an atom. In the case of the H and D atoms, conventional valence theory leads us to suppose that any charge migrations that may take place as a result of the formation of a molecule, will be such as to attract charge into the region between the nuclei. This would be expected to give the appearance of a shorter bond rather than a longer one. Dr. Stoicheff has been very careful not to offer any "explanation" of the effects which he has catalogued and analysed. Does he have any comments to make on the unexpected situation for CH bonds in methane just described?

B. P. Stoicheff

Reply to comments by C. A. Coulson

The discrepancy to which Dr Coulson refers is probably correctly interpreted by Bartell, Kuchitsu and De Neui (reference 31) as arising from the different averages over the zero-point vibrations inherent in the two methods. The above authors have computed corrections to the diffraction "r_g" and spectroscopic "r_0" values (by *assuming* a modified anharmonic Urey Bradley force field) which result in similar *calculated* values of the equilibrium bond length in methane.

The effect which Dr. Coulson mentions while undoubtedly present would perhaps be expected to produce only a small difference in apparent bond lengths. Unfortunately the experimental data and our knowledge of potential functions of polyatomic molecules are too limited to look for such interesting effects. As a first step in understanding the difference between diffraction and spectroscopic values of bond lengths I believe it would be very useful to obtain electron diffraction data on diatomic molecules for comparison with existing spectroscopic data.

D. R. Lide

Comments on the paper by B. P. Stoicheff

DR. STOICHEFF has raised a question about the C—C distance in isobutane. He states that the value of 1·525 Å [*J. Chem. Phys.* 33, 1519 (1960)] might be in error by as much as 0·007 Å because of the small z co-ordinate of the off-axis carbon atoms. In fact, there is no reason to suspect an error of this magnitude. Since almost three-quarters of the total mass of the molecule is in the plane of the off-axis carbons, this plane must necessarily lie close to the center of mass. This type of molecule is clearly distinguished from a case such as propylene, where the central carbon atom lies near a principal axis for rather accidental reasons (i.e. because of an approximate balancing of the other masses in the molecule). As an independent check one may calculate the z co-ordinate of the off-axis carbons from the first-moment relation; the change in the C—C distance is completely trivial (specifically 0·0004 Å).

There is strong evidence, then, that the r_s value of the C—C distance in both isobutane and propane is very near 1·526 Å. The distance in ethane is much less certain.

The values of 1·534 Å and 1·539 Å obtained from infrared and rotational Raman spectra, respectively, do not agree as well as they should. Furthermore, these are mixed r_s and r_0 values, and it has been pointed out that the true r_s distance might be as much as 0·008 Å lower. Thus there is no clear evidence at this time for a discrepancy between the ethane and propane–isobutane values. Ethyl fluoride should be excluded completely from these comparisons. Here the location of the central carbon atom could not be experimentally determined, and it was arbitrarily assigned a co-ordinate of zero. The resulting C—C distance could be in error by as much as 0·02 Å.

B. P. Stoicheff

Reply to comments by D. R. Lide

I AM grateful to Dr. Lide for pointing out the difficulty in the determination of the C—C bond length in ethyl fluoride;[52] a calculation shows the uncertainty in this value to be about 0·010 to 0·020 Å and therefore this bond length should be deleted from Table 3.

The source of this difficulty in the ethyl fluoride structure[52] illustrates my point that the C—C bond length in isobutane may be slightly longer than the quoted value of 1·525 Å. In ethyl fluoride it is found that the moment of inertia *decreases* by 0·0064 a.m.u. Å^2 when ^{13}C is substituted for ^{12}C in the near-axis position. This anomaly is of course a consequence of zero-point vibrations. There is no reason to expect a smaller effect when substitution is made on a C atom no matter what its position in a molecule. Thus if we assume a similar decrease in the moment of inertia in propylene[57] the r_s coordinate for the central C atom becomes 0·112 Å rather than 0·081 Å and is in good agreement with the preferred value of 0·106 Å obtained from the first moment equation.[57] A similar zero-point vibration effect in isobutane leads to a C coordinate of 0·126 Å instead of 0·102 Å and results in a C—C bond length of 1·532 Å. Unfortunately, the evidence from the first moment equation is not completely convincing here because of the assumptions regarding the internal as well as the axial symmetry of three CH$_3$ groups. In conclusion it may be said that the C—C bond lengths in ethane and isobutane are somewhat uncertain but the uncertainties are such as to bring both closer together.

C. A. Coulson

Comments on paper by O. Bastiansen and M. Traetteberg

(1) I SHOULD like to ask Professor Bastiansen whether he can give any reason why the "single" bond in cyclooctatetraene should be 0·021 Å shorter than in butadiene. It is hard to avoid the conclusion that some sort of resonance is operative in the ring molecule, not equally operative in the chain.

(2) Professor Bastiansen has raised the important question of the possible existence of attractive (as well as repulsive) forces between non-bonded atoms such as the halogens in 2,2′-dihalobiphenyls. It may be worth mentioning that in force-constants analysis of the vibrations of several molecules, notably the group V trihydrides, indications of such attractive forces have sometimes been found. If this is indeed the case with the *ortho*-biphenyls then the total potential energy curve as a function of the

angle θ of twist of the two halves, measured from zero in the *cis*-form may sometimes be as shown in the diagram. Here:

curve 1 is the resonance energy curve
curve 2 is the steric repulsion curve
curve 3 is the dispersion (?) attractive force,
with its minimum in the *cis*-position.

The final curve 4 shows minima at some fairly small value of θ, and also at $\theta = \pm\pi$. But they are not of equal height.

O. Bastiansen

Reply to comments by C. A. Coulson

I AM afraid I cannot give a good explanation for the mentioned difference in bond distance. I agree with Professor Coulson that it is difficult to avoid the conclusion that some sort of resonance characteristic for the ring molecule must take place. As stated in our article the effect may perhaps be related to the cyclic form of cyclooctatetraene that might favor *p*-electron delocalization. This "cyclic" resonance effect must be so large as to over-compensate for the loss in resonance due to the less effective *p*-electron overlap in cycloöctatetraene compared to that in butadiene.

W. M. Schubert

Comments on paper by O. Bastiansen and M. Traetteberg

(1) THE finding that the 2,2′-halobiphenyls prefer a near *cis* instead of a near *trans* conformation is a convincing case for the operation of a dispersion force (i.e. van der Waals attractive force). However, it is not clear whether the main attractive force is between an *ortho*-halogen and the π-system of the attached ring (attraction presumably at a maximum for a 90° interplanar angle) or between *ortho*-halogens, although probably the latter. If the latter, the increase in interplanar angle in the order F < Cl < Br < I would speak for an important underlying van der Waals repulsion.

(2) Does the statement to the effect that the planar *trans*-form of 2,2′-bipyridyl should be free of steric strain (also appearing in the paper by Cruickshank) take into account the unshared electron pair on each nitrogen? i.e. what is the van der Waals repulsion radius of the N: as compared to aromatic C—H?

O. Bastiansen

Reply to comments by W. M. Schubert

IN the case of the 2,2′-dihalobiphenyls, we believe the halogen–halogen interaction to be responsible for the near *cis* conformation. It is no doubt correct to include the interaction between the halogen atoms and the π-system of the attached ring; though this interaction is probably less important than the halogen–halogen interaction as also stated by Schubert.

Schubert's question on the 2,2′-bipyridyl is indeed a justified one. In our paper, we were considering the kind of steric hindrance that occurs in the biphenyl derivatives where a planar molecule has to suffer a severe steric strain. What we wanted to express was the fact that the interaction between the two *ortho*-hydrogen atoms is effective only in the *cis* region. In the other possible conformations of the molecule, other effects, such as resonance, should be expected to be predominant. Comparing the two effects to be expected in the *trans* region, namely resonance and hydrogen-nitrogen interaction, our electron diffraction data seem to demonstrate that the resonance energy is not large enough to keep the molecule in the planar form. A possible hydrogen-nitrogen repulsion seems in other words to be of greater importance in the *trans* region conformations than resonance. The hydrogen nitrogen distance in the planar *trans* form is, in fact, a little shorter than the corresponding Pauling van der Waals distance. Without a closer study of the effect, it is difficult to decide in which angle region the van der Waals hydrogen-nitrogen is attractive and in which, if any, it is repulsive. A simple consideration seems indeed to indicate a minor repulsion in the planar *trans* conformation as implicitly suggested in Schubert's question.

I am indeed grateful to Dr. Schubert for having raised this question. The point we wanted to stress, namely the inability of resonance to secure a planar molecule, may have been lost as the effect of our misleading statement. It would no doubt be an interesting undertaking to try to calculate the potential energy as a function of the angle of twist including hydrogen-hydrogen interaction, hydrogen-nitrogen interaction, and resonance.

C. A. Coulson

Comments on paper by D. W. J. Cruickshank

CRUICKSHANK has shown that the simplest of all MO theories gives pretty good results for most bond lengths. But there are residual discrepancies with experiment. It may be mentioned that Dr. A. Golebiewsky and the writer, in some work in course of publication, have shown, using quite simple ideas of self-consistence, that by allowing for the variation of the resonance integral β with bond length, and by including the effect of the underlying σ-bond, the discrepancies can be considerably reduced. In the case of butadiene, which must be regarded as one of the most severe tests of any theory, since the disparity between the short and long bonds is greater than in ring molecules, the theory of Golebiewsky and Coulson reduces the average error from about 0·03 Å to about 0·01 Å. This value seems to be about the best that can be achieved, with theory or experiment, at the moment.

C. A. Coulson

Comments on paper by D. J. Marais, N. Sheppard and B. P. Stoicheff

EVEN if it is agreed that the bond length for the central "single" bond in butadiene is not much shorter than a conventional sp^2—sp^2 trigonal σ-bond, we are still left with the problem of understanding the planarity of butadiene. If butadiene is written as two non-interacting double bonds $^{1}\ \ ^{2}\ \ ^{3}\ \ ^{4}$, then the π-electrons on atoms 2 and 3 would be pairs to other π-electrons (on 1 and 4 respectively) and there would then be the usual repulsion between non-paired electrons which would tend to destroy planarity. Indeed several years ago now, J. Guy [*C. R. Acad. Sci., Paris* **223**, 85 (1946)] showed that this structure, which is merely the conventional Kekule structure for butadiene, would not be planar, since the repulsion of these π-electrons would tend to rotate the two halves relative to each other around the 2—3 bond. This effect is well known for H_2O_2 and N_2H_4, where of course there are two lone-pair electrons on each atom. Even if the argument is not now so strong as it seemed in 1946, it is still true that without some form of conjugation across the central bond it remains rather difficult to understand the high planar stability of butadiene. In present-day views, what is the origin of this stability, if it is not some measure of conjugation?

Is it unreasonable to accept something like the value 1·515 Å. for the pure sp^2—sp^2 σ-bond, as in Bastiansen's paper, applicable to hexaphenylbenzene? If so, there is a shortening of 1·515–1·476 = 0·04 Å. in this central bond.

C. A. Coulson

Comments on paper by L. Oleari

It is at first sight surprising that the single-configuration single-center wave function of Oleari gives so good an energy: and yet the much more complex wave function of Saturno and Parr [*J. Chem. Phys.* **33**, 22 (1960)] on which the paper by Turner *et al.* is based, does not improve it as much as one would have hoped. I believe that the trouble lies essentially in the situation around the four H atoms. For there is a singularity in the Hamiltonian at these points, and so, in the language used by Roothaan and Weiss [*Rev. Mod. Phys.* **32**, 194 (1960)] and Kolos and Roothaan [*Rev. Mod. Phys.* **32**, 205 (1960)], there will be certain cusp conditions to be satisfied by the correct wave-function. It may be shown, in general terms, that at each nucleus where any one electron experiences a nuclear charge Ze, the wave function for any one electron must satisfy the condition

$$\partial\psi/\partial r = -Z\psi,$$

where the left-hand side denotes the mean value of the outward gradient of ψ over the surface of a small sphere surrounding the nucleus. If there is spherical symmetry, then of course $\partial\psi/\partial r$ is independent of angular direction, and we reach the condition easily verified for hydrogenic orbitals:

$$\frac{\partial\psi}{\partial r} = -Z\psi$$

It is exceedingly difficult to represent a function which has a discontinuity of slope at some given point in terms of functions based on some other point as origin. Thus it is to be expected that a large number of terms will be needed to deal with this singularity alone, quite independently of any electron-correlation effects which we know will be important. Precisely this situation has been carefully investigated by M. Cohen and the writer [*Proc. Camb. Phil. Soc.* **57**, 96 (1961)], where, in the case of H_2^+, using a single-centre model, the effect of introducing more and more terms in a trial wave function showed itself almost entirely in a closer approximation near the nuclei. It seems reasonable to hope, therefore, that if the conventional single-centre type of expansion for methane could be supplemented by a single term that would allow for the discontinuity in grad ψ, and more nearly satisfy the cusp condition, considerable improvement in the wave function might be obtained fairly easily. Such a term could be

$$A\{e^{-cr_a} + e^{-cr_b} + e^{-cr_c} + e^{-cr_d}\}$$

where $r_a \ldots r_d$ denotes distances from the four protons. The cusp condition would be that

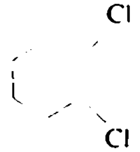
$$\{cA - \psi(0)\}$$

where $\psi(0)$ is the value of ψ at a proton.

C. A. Coulson

Comments on paper by L. S. Bartell

Quite irrespective of whether or not we agree with the particular application of his ideas to the difference between carbon–carbon bonds of varying hybridization, there is no doubt that Bartell is right in drawing attention to the importance of non-bonded interactions. These may be either attractive or repulsive, with repulsive forces usually predominating. The origin of these forces, in any but the simplest pseudo-atomic systems, is exceedingly complex. Thus in the *ortho*-dichloro-benzene molecule, there will be chlorine-chlorine forces of the following kinds:



(i) electrostatic repulsion between effective net charges on the two chlorines,
(ii) attraction due to resonance with structures showing Cl--Cl as a single bond,
(iii) overlap repulsion between the charge-clouds of each separate chlorine atom,
(iv) dispersion forces of attraction between the chlorines,
(v) "random-spin" repulsions of the electrons not paired to each other in the two chlorines,
(vi) interactions due to dipoles and higher multipoles in the C—Cl bonds, and smaller contributions from more remote parts of the molecule.

Some of these forces have been investigated by Stocker and myself (C. A. Coulson and D. Stocker, *Mol. Phys.* **2**, 397 (1959); C. A. Coulson, Chemical Society, Kekule Symposium, London, 1958; Butterworths Scientific Publication).

But the series of contributions (i)–(vi) counts certain types of interaction more than once, and any complete unequivocal separation of the total interaction into contributions of this kind seems at present quite impracticable. It is my impression that the study of these forces between non-bonded atoms may well play a dominant role in molecular-structure calculations of the next ten years.

W. M. Schubert

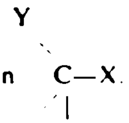
Comments on paper by L. S. Bartell

The intriguing non-bonded interactions hypothesis of Bartell is at least qualitatively consistent with the decrease in C—C bond length with a decrease in the number of substituents on the two carbon atoms. However, the hybridization hypothesis of Dewar and Schmeising seems to more simply accommodate the observation that C—C bond lengths cluster about discrete values according to whether the carbons can be labeled as tetrahedral, trigonal or digonal. Bartell's argument that there is a close balance of the postulated considerable repulsive forces between substituents attached to the same tetrahedral (or trigonal) carbon atom is used to account for C—C shortenings depending apparently only on the *number* of repulsions, and also answers other questions that could be raised. Although Bartell's calculations based on intermolecular van der Waals force laws may indicate there is a balance of repulsive forces, it is nevertheless difficult to imagine why this should be so, i.e. what are the underlying "theoretical" reasons why, e.g. in the variation of say one of the substituents on a tetrahedral or trigonal carbon, the bond length of the varying substituent (of discrete length for any tetrahedral, trigonal or digonal carbon-substituent), the bond angles, and possibly the bond lengths to the remaining fixed substituents (but not for carbon-substituents), should so adjust as to maintain such a balance?

The interesting relief of strain explanation offered for the β-deuterium kinetic isotope effects found by Lewis and by Shiner in solvolysis reactions appears offhand to contradict the balance of repulsion forces argument. That is, the isotope effect is attributed to an *imbalance* of repulsive forces between isotopic species in the tetrahedral ground state and in the transition state, which is on the way to becoming tetrahedral. It is true that only a small imbalance of repulsive forces need be required to account for the small $\Delta H\ddagger$ differences between the isotopic compounds. But if the imbalance created by a considerable substituent change (e.g. hydrogen to chlorine) is supposed to be small, then a change in substituent from hydrogen to deuterium must create an extremely small imbalance of repulsive forces.

L. S. Bartell

Reply to comments by W. Schubert

THE points raised by Dr. Schubert emphasize the need for consideration of the magnitudes of effects involved. His reservations center chiefly upon the forces between X and Y groups in  $\overset{Y\diagdown}{\underset{\diagup|}{C}}\text{—}X$. In reply, it may be said that no such rigid balance is required of the non-bonded model as Schubert implies. The C X bond length and energy may very well vary somewhat with the nature of Y as well as with the number of repulsions. Brief conjectures about this were made in my paper but the documentation of such variations is very meager. Even the principal variations treated in the paper are not much larger than common experimental errors.

A rationalization of the approximate balance (i.e. the relative insensitivity of X. . .Y interactions to the nature of Y) is given in my comments on Professor Wilson's paper. No detailed readjustments of bond lengths and angles of the sort envisioned by Dr. Schubert are required. Several observations suggest that the balance is not exact. If isomerization energies of paraffin hydrocarbons are non-bonded in nature, our model requires $(V_{CC} - V_{HH} - 2V_{CH})$ to be about 1·3 kcal/mole. Bond angles imply similar imbalances.

As a rule X. . .Y forces seem to be of the order of 0·1 md, X. . .Y potential energies of the order of 3 kcal/mole, and C—Y force constants, perhaps a few md/Å. Imbalances of several hundredths md should not seriously invalidate the essence of the simple model. The imbalance involved in the β-deuterium isotope effect, which appeared to Schubert to contradict our hypothesis, is actually only about 0·001 md, and consequently, of no concern in the broad picture. This small distinction between CH_3. . .Y and CD_3. . .Y forces, which is predicted by the non-bonded model, is nevertheless sufficient to account roughly for the observed isotope effect. The difference between the presence of a CH_3 group and its complete absence, as essentially occurs in the comparison of $(CH_3)_2CH$ C and CH_3CH—C, represents a change in C. . .C interactions one hundredfold greater. It was this type of change with which the present work was primarily concerned.

In conclusion, it is fair to remark that the main value of the simple non-bonded model is more in the forceful attention it draws to the possible magnitude of the universally neglected interactions than in its reliable handling of them. It is not difficult to find arguments to the effect that the model may be spurious and that the bond and unshared electron distributions rather than atom-atom interactions must be vitally important. Consider the fact (see reference 28) that the plucking of hydrogen atoms from H_2O, NH_3 or CH_4 lengthens rather than shortens the remaining bonds, even though the number of non-bonded repulsions is reduced. In partial defense of the nonbonded model, it may be mentioned that the resolution of experimental F matrices into components (reference 18) renders this lengthening compatible with the existence of nonbonded repulsions. The stretch-stretch bond interactions imply the correct magnitude of bond lengthening when adjacent bonds are severely stretched. Conversely, they also correctly imply the more easily understood shortenings of bonds when adjacent bonds are shortened, the limit being reached at the united atom stage, HF. Clearly, the non-bonded model must be used with caution.

L. S. Bartell

Comments on the paper by E. Bright Wilson, Jr.

PROFESSOR WILSON'S opinion that the roles of steric influences, conjugation, and hybridization cannot be very definitively assessed at present seems to be shared by many of the contributors to this symposium, including myself. His conclusion in the abstract that "the steric theory is probably untenable", however, appears to me at least as speculative as the steric theory itself, in view of the meager evidence he has cited against it.

The principal virtue of the "steric theory" (or, as I regard it, the hypothesis that *intramolecular* nonbonded interactions follow roughly the same force laws as are ascribed to their *intermolecular* counter parts) is that it correlates, semi-quantitatively, a wide variety of known effects in an extremely simple way. It is as yet far from rigorous, and it must be emphasized that not one correlation it makes is in itself an unequivocal demonstration of the validity of the hypothesis. Therefore, it is of interest to examine Professor Wilson's arguments against the model. They are, as I see them:

(a) Our ignorance of nonbonded potentials is very great.

(b) It would be remarkable if different substituents did not lead to markedly different results.

(c) Barriers to rotation are not steric.

(d) The naive "hard sphere" model of bond angles works no better than the naive hybridization model.

Point (a), of course, cannot rule out the steric model. The balance of repulsions involved in point (b), briefly mentioned in my paper, can be rationalized in terms of Pauling's observation that van der Waals radii are not chaotically scattered but rather are closely related to covalent radii. Pauling's relation, coupled with the usual empirical approximations for nonbonded interactions, suggests a considerable compensation for variations in atomic size of substituents. Larger atoms are associated with correspondingly larger nonbonded distances in the carbon environments of most concern to us. It is fair to admit, however, that the literature dealing with steric interactions is inadequate to settle the exact amount of compensation. Point (c) of Professor Wilson is almost surely true, as he has shown so beautifully in his recent research, but this implies no incompatibility with the steric model. The repulsions I invoke are an order of magnitude *too small*, at least in ethane, to account for the barrier. Finally, the excessive oversimplifications of the models in point (d) render any very subtle comparisons inconclusive. The "hard sphere" model was introduced originally simply to point out that it provides an alternative description to the well-known constant-angle model discussed by Wilson, and one strongly smattering of "steric" influence. Having served as a brief introduction to the idea of intramolecular interactions, it was discarded in the original paper in favor of a model with a more reasonable force law.

Nevertheless, it is interesting to note that the simplest steric model works remarkably well even for the recent data cited by Professor Wilson, except for angles involving hydrogen. If hydrogens are excluded, the angles show a mean deviation of only about 1°, a scatter no greater than the errors in the data from which the sphere radii were assigned. The spectroscopists clearly have difficulty with hydrogen positions (they are not alone in this respect!) and errors of several degrees are not unknown. Accordingly, the poorness of fit with hydrogen may not be solely the fault of the model. On the other hand, the model does not appear sufficiently fundamental to be worth more detailed consideration at present.

Additional evidence that steric effects influence bond angles has been presented by A. I. Kitaigorodskii. (*Abstract G. S.* III 2, Federov Session on Crystallography, Leningrad, U.S.S.R. May 25, 1959) Kitaigorodskii successfully correlated variations in bond angles in a large number of organic molecules using nonbonded potential functions similar to those I invoke. Also, contrary to the first impression of many chemists with regard to the probable direction of steric effects, the fact that the C–C–C angle in isobutane is larger than 109·5° but *smaller* than that in propane [D. F. Lide, *J. Chem. Phys.* **33**, 1514, 1519 (1960)] is accounted for by a steric model, and the presently considered potential functions [L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960)] yield fair quantitative predictions of the angles.

The present nonbonded model is subject to serious criticism in its oversimplified representation of molecular force fields. Nonetheless, the evidence against it seems as yet insufficient to warrant rejecting the basic idea.

W. M. Schubert

Comments on paper by E. B. Wilson, Jr.

With regard to two of Wilson's arguments against the hybridization hypothesis: firstly, a possible role of conjugation in C–X bonds does not necessarily extrapolate to C–C bonds in which no "unshared" electron pairs are involved, as nicely pointed out in the paper by Lide; secondly, the Dewar hypothesis does not require that C–H bond distances vary with hybridization to the same extent as C—C distances. In fact, a smaller variation in C—H bond distances would perhaps be more consistent with the smaller variation in C—H than C–C bond energies that are required in the Dewar hypothesis to account for the stabilization energy of butadiene, etc. In that connection, a smaller variation in the C–H bond energy with hybridization could be due in part to the electronegativity of hydrogen being greater than that of tetrahedral carbon. In that event, that part of the changes in the C–H bond energies from tetrahedral to trigonal to digonal carbon that are due to changes in Pauling-like Δ values would be smaller than considered by Mulliken [*Tetrahedron* 6, 68 (1959)] who used electronegativity order: tetrahedral carbon > hydrogen.

G. L. Caldow and C. A. Coulson

Comments on paper by L. Pauling

IN connection with Pauling's discussion of the repulsive effects of lone-pair electrons on the bond energies of molecules, we should like to report some recent calculations[1] which we have made for the halogen diatomic molecules, and which are concerned with similar effects. In these halogens, the sequence of bond energies (see Table 1) is $F_2 < Cl_2 > Br_2 > I_2$, in which the position of fluorine seems anomalous. We have made some crude valence-bond calculations which seem to suggest that this anomalous sequence arises from the Coulomb term rather than from the exchange term.

TABLE 1. BOND ENERGIES IN THE HALOGEN MOLECULES (kcal/mole)

	F_2	Cl_2	Br_2	I_2
Experimental dissociation energy D	37 7	57 1	45 4	35 6
Calculated Coulomb energy Q (+*ve* for attraction)	10 3	42 8	37 6	30 2
Empirical exchange energy ($D - Q$)	27 4	14 3	7 8	5·4

If the energy of a two-electron homonuclear molecule is written in the conventional way

$$E = 2E_{\text{atom}} + \frac{Q + J}{1 + S^2}$$

it may be transformed to

$$E = 2E_{\text{atom}} + Q + \frac{\eta}{1 + S^2} \tag{1}$$

where η may be called[2] the effective exchange integral, or bond integral, and S is the overlap integral. The bond energy is

$$Q + \eta/(1 + S^2) \tag{2}$$

where Q, the Coulomb energy, is given by

$$Q = \iint \varphi_A(1)\varphi_B(2)\,\{H - 2E_{\text{atom}}\}\,\varphi_A(1)\varphi_B(2)\,d\tau_1 d\tau_2$$

$$S = \int \varphi_A(1)\,\varphi_B(1)\,d\tau_1$$

With a many-electron homonuclear molecule, simple generalizations of (1) and (2) are necessary. The Coulomb energy Q now takes the form

$$Q = \int \psi_A(1,2,\ldots n)\,\psi_B(n+1,\ldots 2n)\,\{H - 2E_{\text{atom}}\}\,\psi_A(1,\ldots n)\,\psi_B(n+1,\ldots 2n)\,d\tau^{2n} \tag{3}$$

There are somewhat similar expressions for J, η and S, though J now includes repulsive

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[1] G. L. Caldow and C. A. Coulson, in course of publication.

[2] S. Fraga and R. S. Mulliken, *Rev. Mod. Phys.* 32, 254 (1960).

exchange interactions between non-paired orbitals, as well as attractive ones between the paired ones. In (3) ψ_A and ψ_B are the leading diagonal terms in each separate determinantal atomic wave function. Thus in the evaluation of Q we have the mutual repulsion of the two separate atomic charge-clouds, together with the attraction of each charge-cloud for the other nucleus, modified of course by the mutual repulsion of the two nuclei. If there is substantial penetration of one charge-cloud by the other, then the attraction terms (which result essentially from the fact that electrons are being pulled towards two nuclei rather than one) may outweigh the repulsions. This is precisely what we have found.

Thus, assuming pure p σ-bonds, and using Slater orbitals with no hybridization, we find the Q-values shown in the table. These are all of such a sign as to contribute positively to the binding energy. What seems to us to be interesting here is that this sequence of Q-values is the same sequence as that of the experimental binding energies, and indeed if we suppose that the difference between the two is due entirely to the effective exchange integral term corresponding to $\eta/(1 + S^2)$ in (1), then we obtain the smooth set of values shown in the last row of the table. There is now no anomaly in the case of F_2.

It would be nice to be able similarly to calculate the effective exchange terms and verify this variation of η. But not only are these terms more difficult mathematically, they are also more strongly dependent on the assumed form of the orbitals, and the extent of hybridization.

Insofar as our present calculations are significant, they suggest that in many-electron molecules, the generalized Coulomb integral may be dominant in determining the variation of bond energy in a related series of molecules. In the case of the halogens, the low value of $Q(F_2)$ is to be associated with the fact, often pointed out by earlier workers, that the size of the valence-shell orbitals is smaller than would be expected on the basis of an extrapolation from the other members of the series. As a result there is less penetration, and less electrostatic attraction. Our conclusions differ somewhat from those for N_2 in Pauling's paper: for it seems that Pauling pays no attention to Q, and throws all the responsibility for bonding on to the exchange terms. In many cases, of course, Q and J will be expected to vary similarly. Further calculations of both quantities for other molecules will be needed to settle precisely which is normally the more important.

L. S. Bartell

Comment on paper by Inga Fischer-Hjalmars

Some time ago, in a study of isotope effects, I made calculations on biphenyl similar to those by Miss Fischer-Hjalmars. Since I used the nonbonded interaction potentials [*J. Chem. Phys.* **32**, 827 (1960)] referred to in my present paper rather than Hills' potentials [*J. Chem. Phys.* **16**, 399 (1948)], it may be of some interest to compare results to illustrate the range of error introduced by our ignorance of the precise form of the potentials. Calculations were made assuming undeformed benzene-like rings with an inter-ring conjugation energy represented by $V_0 \cos^2 \theta$, a function quite similar to that adopted by Miss Fischer-Hjalmars. If V_0 was taken to be 4 kcal/mole, the equilibrium twist angle, using only H. . .H interactions, was found to be about 39° (cf. the experimental value of $42 \pm 10^\circ$). The enhancement of repulsions by zero-point vibrations was found to increase the angle by an additional 1 or 2 degrees (the enhancement for the deuterated species was half a degree smaller). When C. . .H forces were included the angle opened up to about 42°. The equilibrium twist angle was relatively insensitive to V_0, varying by only 5 when V_0 varied by 50%. The potential hill of the planar conformation was appreciably higher than that of Miss Fischer-Hjalmars, being several kcal/mole, but this value was sensitive to the stress-relieving distortions of bond angles anticipated to occur at zero twist.

For several reasons I have reservations about potentials involving hydrogens constructed, as were Hill's, associating a hydrogen van der Waals packing diameter of 2·4 Å with the minimum of a Buckingham or 6-12 potential function. This seems to make hydrogens too small and too "hard". For that matter, my own potentials are essentially based on speculation although they correlate many facts. It is to be hoped that much more attention will presently be given to the calculation of potential functions that we can use with greater confidence.