Ground States of σ-Bonded Molecules. VI.[1] Benzene and Its Isomers. Inductive Effects in Benzene[2]

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Abstract: The MINDO SCF MO method has been used to calculate the heats of formation of benzene, and some of its nonacetylenic isomers. Calculations are also reported for benzene carrying a "pure inductive" substituent, which seem to throw light on the transmission of inductive effects.

The structure and reactivity of benzene and its derivatives have been the subjects of countless experimental and theoretical investigations; until recently, however, the latter have been confined to the π electrons. Calculations of this kind, based on the Hückel σ,π approximation, are limited in scope. In particular, they cannot be used to predict the relative stabilities of the various isomeric hydrocarbons with the molecular formula C_6H_6, nor can they be applied to problems involving the polarization of σ bonds (*i.e.*, typical substituent effects). We therefore thought it of interest to study both of these problems by some procedure in which the σ electrons are explicitly included; the present paper describes such calculations carried out by the MINDO method.[4] This is a semiempirical SCF MO treatment in which the parameters are chosen to reproduce ground-state properties; it has been shown[1,4] to give excellent estimates of the heats of formation of both conjugated and nonconjugated molecules, other than those containing triple bonds.

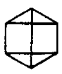
Benzene and Its Isomers

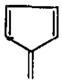
The structure of benzene (I) itself has of course long ceased to be a matter of controversy; however, its various possible valence tautomers have recently returned to the limelight, having been detected as photoisomerization products of benzene or its derivatives. Thus irradiation (253.7 nm) of benzene gives benzvalene[5] (II), while similar treatment of hexamethylbenzene gives hexamethyl derivatives of Dewar benzene (III) and prismane[6] (IV). Dewar benzene itself has, moreover, been synthesized,[7] and its derivatives are now readily accessible by Diels–Alder reactions between cyclobutadiene and derivatives of acetylene.[8] In addition to these valence tautomers, three other cyclic isomers of benzene are also known, *viz.* fulvene (V), bis(methylene)cyclobutene (VI), and tris(methylene)cyclopropane (VII). Indeed, V can be obtained from benzene by photolysis at 184.9 nm.[9]

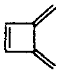

I

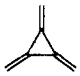

II


III


IV


V


VI


VII


VIIIa, bond lengths 1.483, 1.337 Å
b, bond lengths 1.512, 1.337 Å

Calculations were therefore carried out for the C_6H_6 isomers I–VII, and also for two "classical" models (VIII) for benzene. In the first (VIIIa), the lengths of the single bonds in a Kekulé structure were assumed to be 1.483 Å; in the second (VIIIb) they were assumed to be 1.512 Å. The lengths of the double bonds in each case were taken to be 1.337 Å. The first model corresponds to the structure that would be expected for 1,3,5-cyclohexatriene if the bonds in it were similar to those in an open-chain polyene,[10] while the second corresponds to a "pure classical" structure with "pure single" and "pure double" bonds.[10b,c] Comparison of the energies of I and VIII should be of interest in connection with the problem of defining resonance energies.

Theoretical Procedure and Results

The MINDO method does not lead to good estimates of bond lengths;[4] the calculations are therefore carried out using assumed geometries. These in turn are estimated by using standard values for bond lengths, bond angles, and dihedral angles. The values assumed here for these quantities, and for the various parameters in the treatment, were the same as in part IV;[4] thus the bond lengths in Dewar benzene (III) were assumed to be those appropriate to a four-membered ring, and the angle between the planes of the two rings, and the bridge (C_{sp^3}–C_{sp^3}–H) angle, were each assumed to be 120°. The calculations were carried out using the MINDO program[11] on the CDC 6600 digital computer at The University of Texas. The results are shown in Table I. The third column shows energies of the various isomers, relative to benzene.

Calculations were also carried out for I, and V–VIII, by a method[10b,c] based on the Hückel σ,π approximation, the σ electrons being assumed to be localized and

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[1] Part V: N. C. Baird, M. J. S. Dewar, and R. Sustmann, *J. Chem. Phys.*, in press.

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[3] Robert A. Welch Postdoctoral Fellow, 1966–1968.

[4] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, in press; part IV of this series.

[5] E. E. Wilzbach, J. A. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).

[6] D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966).

[7] E. E. von Tammelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963).

[8] L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, 87, 3253 (1965); L. Watts and R. Pettit, Werner Centennial, Advances in Chemistry Series, No. 62, Washington, D. C., 1966, p 549.

[9] L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **89**, 1030 (1967).

[10] (a) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965); (b) M. J. S. Dewar and C. de Llano, submitted for publication; (c) C. de Llano, Ph.D. Thesis, The University of Texas, Austin, Texas, 1968.

[11] Available from The Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401.

Table I. Heats of Formation (ΔH_f) of Benzene and Its Isomers

Compd	Calcd by the MINDO method, kcal/mol	Relative to benzene		Strain energy, kcal/mol
		MINDO	π procedure	
I	20.2[a]	0	0	
VIIIa	29.9	9.7	7.2[b]	
VIIIb	53.8	33.6	46.8[b]	
II	79.1	58.9		64.6
III	69.7	49.5		34.1
IV	101.1	80.9		107.6
V	39.9	19.7	18.9[b]	0.1
VI	48.7	28.5	23.3[c]	8.9
VII	78.5	58.3	22.4[b]	38.7

[a] Observed 19.8 kcal/mol; see ref 4. [b] See ref 10b,c. [c] Value calculated by Mr. J. Hashmall.

the π electrons treated by an appropriate semiempirical SCF MO procedure; differences between the energies so calculated for I and for its isomers are shown in the fourth column in Table I.

The last column in Table I lists strain energies found by comparing the calculated (MINDO) heats of formation with those given by a modification of Franklin's group additivity method.[12] For our purpose, the values for groups containing the unit C=C had to be modified; for Franklin makes no allowance for changes in the bond energies of C–C σ bonds with the hybridization of the terminal atoms.[13] Thus his value for vinyl is effectively derived by subtracting the group value for methyl from the heat of formation of propene; this corresponds to a situation where vinyl is bonded to a saturated carbon atom. The observed heat of formation (26.33 kcal/mol) of 1,3-butadiene is consequently much less than that (30.00 kcal/mol) given by taking twice Franklin's value for vinyl, the central bond in butadiene being much stronger than the single bond in propene. Accepting the arguments in ref 10, and the bond energies for "polyene-type" bonds deduced there,[10b,c] we arrive at the group values shown in Table II for the various C=C units adjacent to sp^2-hybridized carbon atoms. The strain energies listed in Table I were obtained from heats of formation of unstrained structures estimated using these group values, together with Franklin's values for groups of other types.

Table II. Group Values for Vinyl-Type Groups Adjacent to sp^2 Carbon

Group	Group value (ΔH_f(298°)), kcal/mol
$-CH{=}CH_2$	13.16
$-CH{=}CH-$	13.28
$>C{=}CH_2$	13.28
$>C{=}CH-$	13.40
$>C{=}C<$	13.52

Relative Energies of C_6H_6 Isomers; "Resonance Energy"

The term "resonance energy" has been defined in three distinct ways. In the first, the heat of formation of a given conjugated compound is compared with that estimated for an idealized structure with "pure single" and "pure double" bonds. In the second, the heat of hydrogenation is compared with that of some "model" compound in which the resonance energy is assumed to be zero. In the third, the heat of formation is compared with that predicted for classical structure, in which the "single" and "double" bonds are localized bonds of the type observed in classical polyenes.[10,14]

According to the third definition, the resonance energy of benzene should be equated to the difference between its heat of formation and that of classical cyclohexatriene. The value so found[10b,c] was 0.87 eV, or 20.0 kcal/mol. Comparison with the values listed for VIIIa in Table I indicates that benzene, even when distorted to the geometry expected for cyclohexatriene, still remains more stable than the classical isomer, the resonance energy of VIIIa being about half that of benzene itself. This conclusion is also supported by the π bond orders calculated for the "single" and "double" bonds in VIIIa (0.89 and 0.38, respectively, compared with values of 0.98 and 0.21 in a classical polyene[10]).

The two values for the heat of formation of VIIIb differ significantly; much of this difference can be attributed to an error in the MINDO value. The MINDO method leads to predicted bond lengths which are much too small; it is therefore parametrized to give good heats of formation for molecules in their observed geometries, rather than in the equilibrium geometries calculated by the MINDO method itself. The derivatives of the energy with respect to bond lengths, angles, etc, will then have finite values for the assumed ground-state geometry, instead of vanishing, as of course they would do if the calculated equilibrium bond lengths, etc., were the same as those observed. Consequently any attempt to calculate the energy required to deform the molecule into a nonequilibrium state, using the MINDO method, will lead to values which need not, and probably will not, bear any close relation to reality. One cannot therefore arrive at meaningful estimates of the energies of nonequilibrium configurations by procedures of this kind; for such purposes it is *essential* to have a treatment that gives good estimates both of heats of formation and of molecular geometries.[15]

The π procedure on the other hand does meet both criteria. The heats of formation, and bond lengths, predicted in this way for a very wide range of conjugated molecules agree closely with experiment.[10b,c] Indeed, in the case of benzene, it even leads to a very good estimate of the force constant for the symmetrical breathing vibration, implying that the curvature of the

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(12) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(13) *Cf.* M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); 11, 96 (1960).

(14) M. J. S. Dewar, *Chem. Eng. News*, **43** (2), 86 (1965); *Tetrahedron Suppl.*, 8, 75 (1966).

(15) This point should perhaps be emphasized, since a number of papers have recently appeared in which potential energy surfaces are calculated by methods which fall far short of satisfying either criterion. Although it is of course conceivable that the results might correspond to reality, at least in some cases, through a fortuitous cancellation of errors, there is certainly no evidence that this is the case. Such evidence could be afforded by calculations for nonequilibrium configurations that can be studied experimentally; calculations of force constants for molecular vibrations could for example provide such a test. At present, however, no significance can be attached to such calculations of potential energy surfaces, or to attempts to draw deductions from them concerning the structures of transition states or the mechanisms of reactions. It cannot even be argued that the attitude taken here is a Eutopian one, and that meaningless calculations have a place on the grounds that meaningful ones are far out of reach; for our own investigations alone have shown very clearly that suitable semiempirical SCF MO techniques can be, and soon will be, developed.

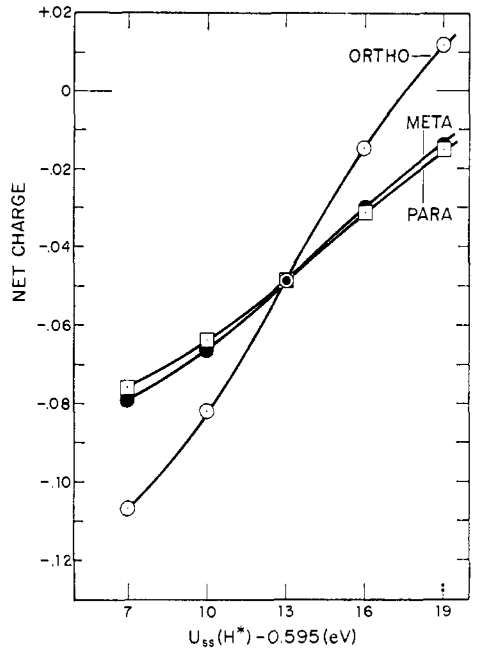

Figure 1. Changes in net charge at the hydrogen atoms in $C_6H_5H^*$ as a function of $U_{ss}(H^*)$.

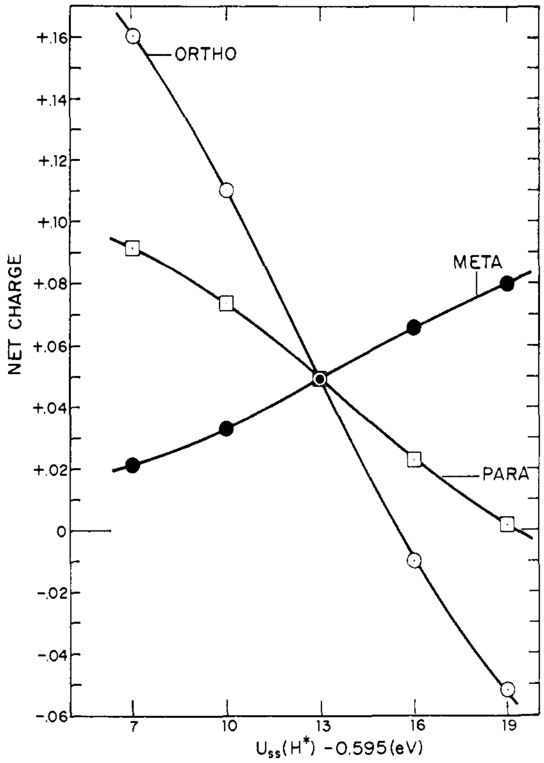

Figure 2. Changes in net charge at the carbon atoms *ortho*, *meta*, and *para* to H* in $C_6H_5H^*$ as a function of $U_{ss}(H^*)$.

potential energy surface near equilibrium is correctly reproduced. The heat of formation estimated in this way for VIIIb is therefore probably close to the truth. Incidentally this value is almost identical with that predicted for a "pure classical" structure VIIIb with "pure single" and "pure double" bonds, using the bond energies of ref 10b,c; the corresponding difference in energy (46.8 kcal/mol) between I and VIIIb can therefore be taken as a measure of the "conventional" resonance energy of benzene according to the first definition above.

The remaining isomers of I are all predicted to be very much less stable than benzene itself; their observed behavior seems to be consistent with the predicted heats of formation. Thus fulvene (V) seems to be the least reactive, followed by bis(methylene)cyclobutene (VI) and tris(methylene)cyclopropane (VII), while prismane (IV) seems to be much the least stable of the valence tautomers of benzene; prismane itself has not yet been prepared. Note that the instability of prismane (IV) and of benzvalene (II) is predicted to be entirely due to ring strain; the "strainless" heats of formation predicted by Franklin's method are more negative than that of benzene. The estimated strain energies of II and III seem to be of the right order of magnitude, considering that the strain energy of cubane is 157 kcal/mol;[16] now that benzvalene (II) and Dewar benzene (III) are available, it is to be hoped that their heats of formation will soon be measured.

The strain energy calculated for bis(methylene)cyclobutene (VI) must on the other hand be too small, considering that the strain energies of cyclobutane and cyclobutene are 26.1 and 26.0 kcal/mol, respectively. The discrepancy cannot be due to an unexpectedly large "resonance" stabilization since the heat of formation predicted for VI by the π method is close to that estimated from the group values in Table II. A similar but smaller discrepancy probably occurs in fulvene (V); it is difficult to believe that V can be almost strain free. The trouble here probably lies in the use of standard single and double bond lengths (1.483 and 1.337 Å, respectively) in the MINDO calculations; the bond lengths in cyclobutane are known to be longer than usual, and allowance had to be made for this in part IV;[4] the corresponding values for bonds in a conjugated four-membered ring are not known. Note that the strain energy (38.7 kcal/mol) predicted for VII is of a reasonable magnitude; a recent electron diffraction study[17] of VII gave bond lengths which differed by only 0.030 and 0.006 Å from our assumed values, the differences being little more than the estimated experimental error (±0.02 Å). Here again thermochemical studies would be of great interest.

Inductive Effects in Benzene

Recently Pople and Gordon[18] presented CNDO/2 calculations for a wide range of nonconjugated organic molecules and remarked that the calculated charge distributions are qualitatively different from those that would be predicted on the basis of classical inductive effects; in particular, the charges induced by a substituent alternate along a chain of carbon atoms instead of dying away exponentially. Since so much of the work on substituent effects has been based on benzene derivatives, we thought it of interest to see whether or not a similar alternation would be expected to occur in benzene carrying a "pure inductive" substituent. We have therefore carried out some MINDO calculations for systems of this type.[19]

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(16) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966).

(17) E. A. Dorko, J. L. Hencher, and S. H. Bauer, *Tetrahedron*, **24**, 2425 (1968).

(18) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

(19) It should be mentioned that our MINDO calculations[1,4] for nonconjugated systems predict the same type of charge alternation as that found by Pople and Gordon in their CNDO/2 approach.

We are interested here in purely inductive substituent effects, *i.e.*, the effect arising from polarity of the σ bonds linking a substituent to one atom in a benzene ring. Real substituents can, however, also exert conjugative effects and it would be difficult to disentangle these from concomitant inductive contributions; in order to study the latter in isolation, we therefore introduced a hypothetical substituent termed H*, the properties of which are identical with those of a hydrogen atom apart from one-center core attraction integral U_{ss}[4].

MINDO calculations were carried out for $C_6H_5H^*$ for various values of $U_{ss}(H^*)$; the response of the net charges on the hydrogen atoms is indicated in Figure 1. The signs of the changes in net charge correspond to those expected for a classical inductive effect, an increase in the electronegativity of H* (represented by a decrease in U_{ss}) leading to a decrease in net charge at all positions; this result is entirely different from that observed in nonconjugated systems.

The relative magnitudes of the changes in net charge at the *ortho*, *meta*, and *para* positions (2.0:1.1:1) are very close indeed to the ratios (2.0:1.15:1) predicted according to a simple classical model for the interaction, assuming the "inductive effect" to be propagated directly across space (*i.e.*, a field effect) rather than by successive polarization of bonds.[20] Indeed, the calculated charge densities suggest that the classical "inductive effect" is attenuated very rapidly, its effect being negligible after the carbon atom linked to H*. The change in electronegativity of this carbon atom does, however, lead to a polarization of the π electrons (π-inductive effect) and this in turn leads to an alternation of induced charge around the ring; thus an increase in electronegativity of H* leads to positive induced charges in the positions *ortho* and *para* to it but to negative ones in the *meta* positions, the charges being in the ratio 20:−4:1 (Figure 2). Note that this charge alternation is not transmitted to the adjacent hydrogen atoms. The alternation is due to a polarization of the π electrons in the ring, and there is apparently little transmission of this to the CH σ bonds. This again emphasizes the low efficiency with which classical inductive effects are propagated; polarization of the π bonds to a given carbon atom apparently has little effect on the other (σ) bonds formed by it.

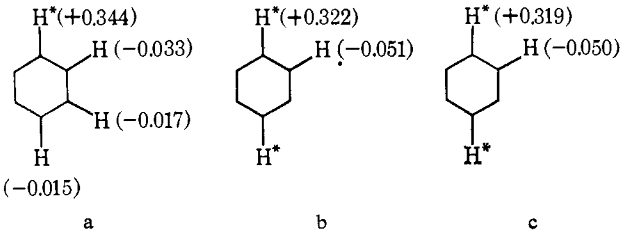

Figure 3. Changes in charge densities calculated by the MINDO method ($U_{ss}(H)$ = −10.6 eV; $U_{ss}(H^*)$ = −13.6 eV) for (a) $C_6H_5H^*$ and (b) p-$C_6H_4H_2^*$; (c) shows charges calculated on the basis of additivity, using the results in a.

In the absence of interfering conjugative interactions, substituent effects in benzene are found to be additive. In order to see if the same would hold for the charge densities given by our MINDO calculations, we also studied the disubstituted benzenes $C_6H_4H^*_2$. The MINDO changes in net charge indeed agreed within 2% with those calculated on the basis of additivity, using the charges predicted for $C_6H_5H^*$; this result held for all three isomers of $C_6H_4H^*_2$ over the whole range of values for $U_{ss}(H^*)$. A typical example is shown in Figure 3.

This result would of course be expected if long-range "inductive effects" are in fact due to direct electrostatic interactions across space; deviations from additivity would be expected to occur only in cases where the polarizations are very large.

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(20) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

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d-Orbital Effects in Silicon-Substituted π-Electron Systems. XV.[1] The Color of Silyl Ketones

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Contribution from the Institute of Inorganic Chemistry of the University of Munich, Munich, Germany. *Received May 3, 1968*

Abstract: Relative to the colorless dialkyl ketones the n → π^* transition energies of the yellow monosilyl and the violet disilyl ketones are considerably lowered. To elucidate the influence of R_3Si groups on the carbonyl chromophore, vertical ionization energies, charge-transfer maxima, half-wave reduction potentials, and electronic transitions of alkyl and silyl derivatives of phenyl or naphthyl ketones have been measured and assembled in an approximate experimental MO scheme. The energy differences can be rationalized in terms of both strong inductive effects $+I_{Si} > +I_C$ on the oxygen lone pair n_O and additional electron back-donation $Si \leftarrow C_\pi$ in the excited states, as well as in the ground state.

In 1957 Brook[2] synthesized triphenylsilyl phenyl ketone which in contrast to the analogous carbon compound is yellow. Since then, numerous yellow monosilyl and disilanyl derivatives[3-7] and one violet disilyl

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(1) Previous communication, H. Bock, H. Alt, and H. Seidl, *Angew. Chem.*, **80**, 906 (1968); *Angew. Chem. Int. Ed. Engl.*, **7**, 885 (1968).

(2) A. G. Brook, *J. Amer. Chem. Soc.*, **79**, 4373 (1957).

(3) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960); A. G. Brook and J. R. Pierce, *Can. J. Chem.*, **42**, 298 (1964).