Model Studies of Nitrogen–Nitrogen Spin–Spin Coupling Constants

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Abstract: A study of the one-bond nuclear spin–spin coupling constant $^1J_{^{15}N^{15}N}$ has been made using semiempirical coupled Hartree–Fock perturbation theory for the evaluation of Fermi contact, orbital, and spin-dipolar terms. Using hydrazine as a reference system the effects on $^1J_{NN}$ of pyramidization and protonation of one or both nitrogens and of dihedral angle variation were explored. For hydrazines we predict a strong dihedral angle dependence of the coupling constant leading to the possibility of both positive and negative $^1J_{NN}$ depending on conformation. An interpretation of this effect as originating in quantum mechanical interference between lone pair contributions to $^1J_{NN}$ is given. In addition, the various bent and protonated hydrazines discussed here are suitable model compounds for substituted hydrazines such as nitramines.

I. Introduction

Nuclear spin–spin coupling constants between directly bonded nitrogens have received little experimental[1a–c] and even less theoretical attention.[2] Since most of the few known $^1J_{NN}$ values for NN single bonds occur in molecules not completely characterized geometrically and often in nitramines whose oxygen lone pairs may engender their own peculiarities, it seemed appropriate to undertake at this time a model study of the effects on $^1J_{NN}$ of internal rotation about the N–N bond, nitrogen pyramidization(s), and protonation(s) in some simple $>$N–N$<$ containing molecule. Hydrazine, N_2H_4, was a suitable molecule since its geometry is reasonably well characterized[3] and it was also small enough to allow a substantial number of model calculations. Although $^1J_{NN}$ of hydrazine (or its alkyl derivatives) is unknown, the value could, in principle, be obtained for doubly ^{15}N-enriched hydrazine. The magnitudes of $^1J_{NN}$ in several para-substituted phenylhydrazines have recently been determined.[4]

The point of departure of the present work was prior studies[5a,b] of the one-bond carbon–nitrogen spin–spin coupling constant, $^1J_{^{13}C^{15}N}$. In that case, using coupled Hartree–Fock perturbation theory implemented semiempirically for the Fermi-contact ($^1J^{Fc}$), orbital ($^1J^{o}$), and spin-dipolar ($^1J^{sd}$) terms, it was possible to obtain a good account of the signs and magnitudes of all known CN coupling constants. In addition, the following conclusions pertinent to $^1J_{NN}$ were drawn:

(i) For CN single and double bonds the Fermi-contact term usually dominates the sum of the orbital and spin-dipolar terms and is negative, corresponding to the negative product of gyromagnetic ratios, $\gamma_{^{15}N}\gamma_{^{13}C}$.

(ii) When the nitrogen contains an s-hybridized lone pair (as opposed to none in a quaternized nitrogen or a lone pair that is pure p) there is an algebraic increase in $^1J^{Fc}{}_{^{13}C^{15}N}$, which we have termed the *one-bond lone-pair effect*. Thus, occasionally (i) is violated and $^1J_{^{13}C^{15}N}$ becomes positive due to a large positive Fermi contact term, or it is determined in sign by the orbital and spin-dipolar terms if $^1J^{Fc}$ is sufficiently small.

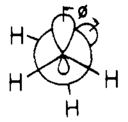
For the $>$N–N$<$ moiety it is possible that the analogues to (i) and (ii) will be found, however, with opposite signs to $^1J_{^{13}C^{15}N}$ since $(\gamma_{^{15}N})^2 > 0$. Moreover, with two lone pairs on different atoms there are now the new possibilities of either additive or quantum mechanical interference effects in the contribution of the lone pairs to $^1J_{NN}$. The latter would perhaps be manifest in a dependence of $^1J_{NN}$ on dihedral angle. Indeed, there is a growing literature[6a] on the dihedral angle dependence of the one-bond phosphorus–phosphorus coupling constant, $^1J_{PP}$, originating with Cowley and White;[6b] a recent theoretical study by Albright and Gray[7] on $^1J_{PN}$ has uncovered similar effects. The present study includes a larger variety of systems and geometry variations than the phosphorus theoretical studies and the results obtained here for $^1J_{NN}$ will therefore be of some interest to experimentalists involved with $^1J_{PP}$ and $^1J_{PN}$.

II. Molecules and Conformations Studied

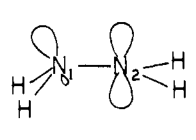
The method of calculation is the semiempirical (INDO type) coupled Hartree–Fock perturbation theory which has been described previously.[5] Two atomic semiempirical parameters, $S_N{}^2(0)$ and $\langle r^{-3}\rangle_N$, are required and, owing to the paucity of experimental data, the atomic values 4.77 $a_0{}^{-3}$ and 3.10 $a_0{}^{-3}$ were employed; ultimately, sufficient experimental data for geometrically characterized NN systems will enable a least-squares determination of $S_N{}^2(0)$ and $\langle r^{-3}\rangle_N$ appropriate to the molecules involved.

Hydrazine has a dihedral angle ϕ between lone pairs of 90–95°[3] (the gauche effect[8]) in its experimentally determined equilibrium geometry. The remaining geometric parameters which probably vary weakly with conformation are the NN and NH bond lengths, 1.45 and 1.02 Å, respectively, and an NNH angle of 112°, the HNH angle (and therefore the extent of nitrogen pyramidization) being unknown, though probably similar to that in ammonia and alkylamines. In view of the slightly different geometries that might be anticipated for substituted hydrazines[9] the following "standard" parameters were employed unless otherwise indicated: NN = 1.47 Å, NH = 1.04 Å, and ∠NNH = ∠HNH = 108°. No small changes in bond lengths or bond angles as might occur between various hydrazine derivatives would seriously alter the qualitative conclusions drawn here. (At this geometry with ϕ = 90° INDO localized orbital NN, NH, and lone-pair hybrids were $sp^{3.9}$, $sp^{3.2}$, and $sp^{1.7}$, respectively).

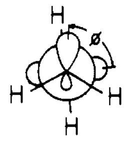
For hydrazine (I) the angle ϕ was varied from 0° to 180° in 30° increments to give seven $^1J_{^{15}N^{15}N}$ values. In addition to I which has two s-hybridized lone pairs it was of interest to study systems with one s-hybridized lone pair, both to obtain the analogue of many such $^1J_{CN}$ values and to furnish a basis for interpreting lone-pair interactions. Such a system could be obtained from I by forcing one of the nitrogens into planarity to give IIa with lone pairs eclipsed (ϕ = 0°) or the general conformer IIb. Calculations of $^1J_{NN}$ in IIb were made for ϕ = 30, 60, and 90°. There are some x-ray data[10] suggesting



I



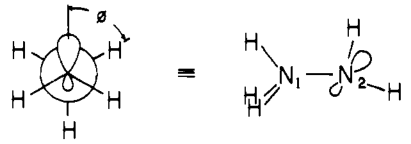
IIa



IIb

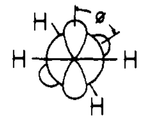
circumstantially that the ring nitrogen of phenylhydrazine is trigonal planar; however, a stronger case can be made for this geometry in *p*-nitrophenylhydrazine.

A second way to eliminate one of the s-containing lone pairs of I is by quaternization of one of the nitrogens. Indeed, the $N_2H_5^+$ ion is known in the form of its chloride and bromide salts. A reasonable structure for the cation would be IIIa since it is isoelectric with methylamine, CH_3NH_2; now, ϕ is the dihedral angle between the lone pair on N_2 and a given N_1H bond. Since previous studies[5c] of CH_3NH_2 showed no appreciable dihedral angle dependence only a single calculation of $^1J_{NN}$ (at $\phi = 120°$) was performed for IIIa.

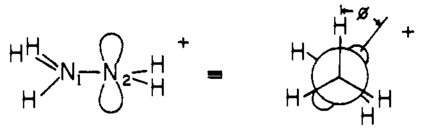


IIIa

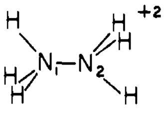
Finally, it was possible to create from hydrazine (I) systems with no s-hybridized lone pairs by: (1) forcing both N_1 and N_2 of hydrazine into planarity with $\angle HN_1H = \angle HN_2H = 120°$ (or alternatively further modifying N_1 of IIb) to give IV containing two pure p lone pairs (calculations on this system were made for $\phi = 0$ (planar hydrazine), 45, and 90°; the planar case is a model for dialkyl nitramines); (2) forcing the NH_2 nitrogen of $N_2H_5^+$ into planarity to give IIIb with an HN_2H angle of 120° (and an attendant increase in the INDO total energy) (given the independence of $^1J_{CN}$ of methylamine on ϕ^{5c} a study of this variable did not seem imperative; nonetheless calculations were made for $\phi = 0$, 15, 30, and 90°); (3) diprotonating hydrazine (or alternatively, protonating N_2 of IIIa) to give the $N_2H_6^{+2}$ dication known as its dichloride salt (as this ion is isoelectronic with ethane and contains no s-hybridized lone pairs only a single $^1J_{NN}$ calculation was made, using staggered arrangement V).



IV



IIIb



V

III. Results

Table I contains the values of $^1J_{^{15}N^{15}N}$ for the above systems from which the following can be seen:

(1) For the systems with *no* s-hybridized lone pairs (IIIb, IV, and V) $^1J_{NN}$ is positive due to a large positive Fermi contact term, analogous to results for $^1J_{CN}$ in similar systems. Furthermore, no dihedral angle dependence was found in the contact contribution for IV, although a dihedral dependence does occur in the ineffectual orbital and spin-dipolar terms.

Table I. $^1J_{^{15}N^{15}N}$ of Hydrazine and Protonated Hydrazines in Various Conformations (Hz)

Molecule	Dihedral angle ϕ, deg	J^{Fc}	J^{o}	J^{sd}	$^1J^{tot}$
Two s-Hybridized Lone Pairs					
Hydrazine (I)[a]	0	−11.9	0.3	0.8	−10.8
(both nitrogens	30	−11.1	0.1	0.7	−10.3
pyramidal)	60	−8.5	−0.2	0.7	−8.0
	90	−3.8	−0.3	0.7	−3.4
	120	2.6	−0.1	0.8	3.3
	150	8.7	0.3	0.9	9.9
	180	11.3	0.4	1.0	12.7
One s-Hybridized Lone Pair					
Hydrazine (II)[b]	0	−3.5	0.8	0.8	−1.9
(N_1 pyramidal,	30	−3.1	0.5	0.7	−1.9
N_2 planar)	60	−2.4	−0.1	0.5	−2.0
	90	−2.1	−0.4	0.4	−2.1
$N_2H_5^+$ (IIIa)[c]	120	−8.0	−0.1	0.5	−7.6
(N_2 pyramidal)					
No s-Hybridized Lone Pairs					
$N_2H_5^+$ (IIIb)[d]	0[g]	3.4	0.0	0.5	3.9
N_2H_4 (IV)[e]	0	11.4	1.6	0.9	13.9
(both nitrogens	45	11.0	0.5	0.5	12.0
planar)	90	10.6	−0.5	0.4	10.5
	0[h]	16.7	1.7	1.0	19.4
$N_2H_6^{+2}$ (V)[f]		2.1	0.2	0.6	2.9
(staggered)					

[a] NN = 1.47 Å, NH = 1.04 Å, $\angle NNH = \angle HNH = 108°$. [b] Same as *a* except $\angle HN_2H = 120°$. [c] NN = 1.45 Å, N_1H = 1.03 Å, N_2H = 1.014 Å, tetrahedral angles at N_1, $\angle HN_2H = \angle HN_2N_1 = 107°$. [d] Same as *c* except $\angle HN_2H = \angle HN_2N_1 = 120°$. [e] NN = 1.47 Å, NH = 1.04 Å, 120° angles at N_1 and N_2. [f] NN = 1.42 Å, NH = 1.048 Å, tetrahedral angles at N_1 and N_2. [g] To the accuracy reported identical results were obtained for ϕ = 15, 30, and 90°. [h] Same geometry as for planar trigonal N_2H_4 except with HNH angles of 108°.

(2) When *one* s-hybridized lone pair is present the sign of $^1J_{^{15}N^{15}N}$ is *negative*, owing to a large negative Fermi contact term. Thus, the *one-bond lone-pair effect* is present in NN coupling as it is in CN coupling, although a change in sign from positive for no s lone pairs to negative for one s lone pair may prove to be the rule rather than the exception. A slight dihedral angle dependence was found for each of the three contributions to $^1J_{NN}$ of IIb; however, these variations largely canceled leaving $^1J_{NN}$ essentially independent of dihedral angle.

(3) In the case where there are *two* s-hybridized lone pairs, namely I and probably its substitutional isomers as well, there is a strong dihedral angle dependence and $^1J_{NN}$ can be either positive or negative. Thus, $^1J_{NN}$ varies from −10.8 Hz at ϕ = 0° to 12.7 Hz at 180°, passing through zero at approximately 115° as depicted in Figure 1. Given that both the INDO equilibrium ϕ, 60°, and the experimental value, 90–95°,[3] are both less than 115° it seems likely that $^1J_{NN}$ of hydrazine is negative. Model calculations on the two conformers of methylhydrazine which have a lone pair dihedral angle of 90° give negative $^1J_{NN}$'s similar in magnitude to that of hydrazine.[5c]

IV. Discussion

It is of interest to consider the origin of the strong dihedral angle dependence of the hydrazine Fermi contact term. As is well known[11] second-order energies, of which J^{Fc} is an example (in units of frequency), in coupled or uncoupled Hartree–Fock

Table II. Contributions to the Fermi Contact Term (in Hz) and INDO Orbital Energies (in au) from the Occupied Valence Orbitals for Various ϕ[a]

Occupied orbital	ϕ = 0°	30°	60°	90°	120°	150°	180°
			Contributions to J^{Fc}				
1	12.0	12.5	13.8	15.5	17.2	18.5	19.0
2	−10.1	−10.7	−12.1	−13.8	−15.4	−16.7	−17.1
3	0.0	−0.3	−1.1	1.4	0.7	0.2	0.0
4	2.4	2.4	2.1	−2.1	−3.5	0.2	0.2
5	0.0	−0.4	−0.2	−0.1	0.1	−5.7	−13.6
6	2.6	3.2	5.6	−14.3	−11.5	−8.3	0.0
7	−18.6	−18.1	−16.6	9.6	15.1	20.5	22.8
Total J^{Fc}	−11.7	−11.4	−8.5	−3.8	2.7	8.7	11.3
			Orbital Energies[b]				
1	−1.56	−1.55	−1.55	−1.55	−1.55	−1.54	−1.54
2	(−1.12)	(−1.12)	(−1.12)	(−1.13)	(−1.13)	(−1.13)	(−1.13)
3	[−0.86]	(−0.85)	(−0.82)	−0.80	−0.83	−0.84	[−0.85]
4	−0.75	−0.75	−0.77	(−0.78)	(−0.73)	−0.68	−0.68
5	[−0.62]	−0.65	−0.67	−0.68	−0.68	(−0.68)	(−0.64)
6	−0.59	−0.56	−0.52	(−0.49)	(−0.53)	(−0.58)	[−0.62]
7	(−0.43)	(−0.44)	(−0.46)	−0.48	−0.45	−0.43	−0.42

[a] Slight discrepancies of the total values from those in Table I are due to roundoff error. [b] Orbital energies in parentheses indicate that the orbital has nitrogen 2s coefficients of opposite sign, while orbital energies in square brackets indicate zero 2s coefficients. In all cases where the contribution to J^{Fc} is large its sign is positive for orbitals whose 2s coefficients are of the same sign and negative for orbitals of oppositely signed coefficients.

perturbation theories are additive in contributions, $J^{Fc}(i)$, from the occupied orbitals, e.g.,

$$J^{Fc} = \sum_{i=1}^{\text{occ MO's}} J^{Fc}(i) \qquad (1)$$

Table II contains the seven valence molecular orbital contributions as a function of ϕ as well as the corresponding INDO occupied orbital energies, e_i. It can be seen that only four orbitals have significant $J^{Fc}(i)$, namely i = 1, 2, 6, and 7 (except for 150° where there is strong mixing of orbitals 5 and 6, and for 180° where there has been an apparent crossing of 5 and 6). The other orbitals have small nitrogen 2s coefficients and therefore small $J^{Fc}(i)$'s.

The sign of $J^{Fc}(i)$, aside from some small exceptions, is positive when the nitrogen 2s coefficients of orbital i have the same sign and negative when they are opposite.[12] This is the result one would anticipate from the uncoupled perturbation theoretical expression in the present integral approximations[5]

$$J^{Fc}(i) \propto C_{2s_{N_1,i}} C_{2s_{N_2,i}} \sum_{j}^{\text{unocc}} C_{2s_{N_1,j}} C_{2s_{N_2,j}} (e_i - e_j)^{-1} \qquad (2)$$

if the important unoccupied orbital(s) j is N–N antibonding and therefore has $C_{2s_{N_1,j}} C_{2s_{N_2,j}} < 0$, which seems to be the case. The contributions from orbitals 1 and 2 are logically taken together as these orbitals are the plus and minus combinations of HN_1H and HN_2H fragments. From Table II, $J^{Fc}(1) + J^{Fc}(2)$ can be seen to be almost completely independent of ϕ having the value 1.8 ± 0.1 Hz. Thus, the dihedral angle dependence of the hydrazine Fermi contact term resides almost exclusively in orbitals 6 and 7 (or more precisely, 5 and/or 6, and 7; vide supra), essentially bonding and antibonding combinations of nitrogen lone pairs, $n_{\pm}$, respectively.

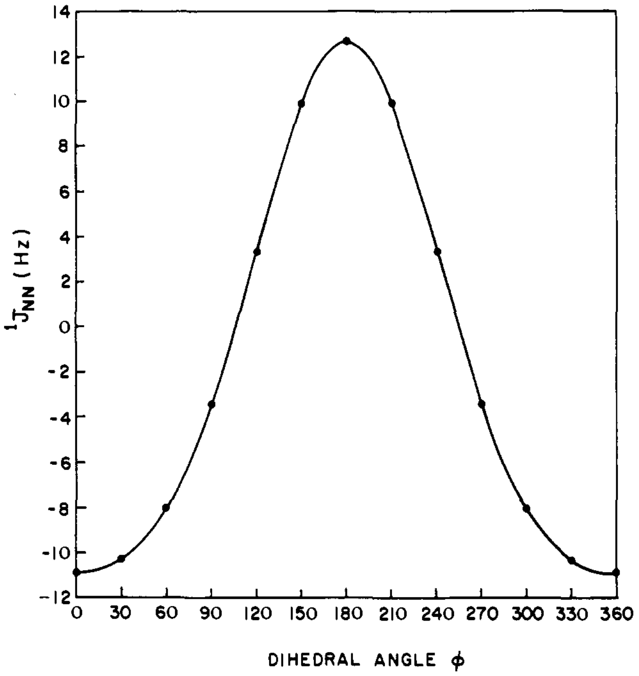
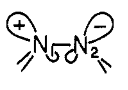
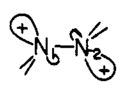


Figure 1. $^1J_{^{15}N^{15}N}$ of hydrazine (1) as a function of dihedral angle ϕ between nitrogen lone pairs.

With reference to eq 2, orbital 7, n_-, should generally make the most important contribution to J^{Fc} since it has the smallest energy denominator (barring, of course, large changes in the magnitudes of the coefficients in the numerator, which do not seem to be occurring here). It is important to realize that, as in the case of diazene,[13,14] the destabilizations relative to n_+ of the antibonding orbital 7, n_-, for both small ϕ (VIA)[15] and large ϕ (VIb) are comparable as evidenced by the comparable bonding-antibonding orbital energy gaps at 0 and 180°. Moreover, from the signs and orientations of the hybridized lone pairs in VIa it can be seen that for small ϕ n_- contains nitrogen 2s coefficients of unlike sign ($C_{2s_{N_1,7}} C_{2s_{N_2,7}} < 0$) and therefore from eq 2 $J^{Fc}(7)$ is negative. Similarly it can be seen from VIb that for large ϕ the 2s coefficients in n_- are of the



VIA



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same sign ($C_{2s_{N_1,7}}C_{2s_{N_2,7}} > 0$) and $J^{Fc}(7)$ is positive. Between 60 and 90° the splitting of bonding and antibonding orbital energies vanishes and the contributions of n_+ and n_- become comparable; thus, in this region the sum $J^{Fc}(6) + J^{Fc}(7)$ vanishes.

Although these qualitative arguments, based on uncoupled rather than coupled perturbation theory, that is, excluding effects of correlation energy in first order cannot furnish the exact angle at which $J^{Fc}(6) + J^{Fc}(7)$ is equal to zero, they are consistent with the angle being nearer to 90° than to 60°. Thus, the dihedral angle dependence of the Fermi contact term in hydrazine has a straightforward interpretation.

Finally, we might point out that since the dihedral angle dependence of the contact term (and therefore also the total J_{NN}) of hydrazine is due to the interaction between lone pairs which ought to vary with the cos ϕ, $J^{Fc}(\phi)$ should be of the form of a power series in cos ϕ dominated by its leading terms

$$J^{Fc} \approx a_0 + a_1 \cos\phi + a_2 \cos^2\phi \qquad (3)$$

From the present semiempirical calculations we obtain with least-squares coefficients: $a_0 = -3.8$ Hz, $a_1 = -11.5$ Hz, and $a_2 = +3.5$ Hz. It is probable that similar functional forms will hold for other cases of *one-bond* coupling constants with two s-hybridized lone pairs.

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References and Notes

(1) (a) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964); (b) N. N. Bubnov, K. A. Bilevitch, L. A. Poljakova, and O. Yu Okhlobystin, *J. Chem. Soc., Chem. Commun.*, 1058 (1972); (c) S. Bulusu, J. R. Antera, and T. Axenrod, *ibid.* 602 (1973); and T. Axenrod and G. A. Webb, "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons," Wiley, New York, N.Y., 1974.
(2) A. R. Farminer and G. A. Webb, *J. Mol. Struct.*, **27**, 417 (1975).
(3) (a) Y. Morino, T. Ijima, and Y. Murata, *Bull. Chem. Soc. Jpn.*, **33**, 46 (1960); (b) T. Kasuya and T. Kojima, *J. Phys. Soc. Jpn.*, **18**, 364 (1963). The rotational barrier is 3.15 kcal/mol.
(4) T. Axenrod and P. Mangiaracino, private communication.
(5) (a) J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.*, **98**, 4701 (1976); (b) J. M. Schulman and T. Venanzi, *ibid.*, **98**, 6739 (1976); (c) unpublished results.
(6) (a) J. P. Albrand, H. Faucher, D. Gagnaire, and J. B. Robert, *Chem. Phys. Lett.*, **38**, 521 (1976); (b) A. H. Cowley and D. W. White, *J. Am. Chem. Soc.*, **91**, 1913 (1969).
(7) T. Albright and G. Gray, private communication.
(8) S. Wolfe, *Acc. Chem. Res.*, **3**, 102 (1970).
(9) Some geometrical parameters for hydrazine derivatives including $N_2H_5^+$ and $N_2H_6^{2+}$ are given: *Chem. Soc., Spec. Publ.*, **No. 18** (1964).
(10) S. Srinivasan and S. Swaminathan, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **127**, 442 (1968).
(11) J. I. Musher, *J. Chem. Phys.*, **46**, 3649 (1967).
(12) For all ϕ there is a C_2 axis present. Therefore $C_{2s_{N_1}} = +/- C_{2s_{N_2}}$ for orbitals of a/b symmetry, respectively.
(13) (a) M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962); (b) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, **90**, 1501 (1968).
(14) Since the same physical arguments apply in the case of diazene, it is not surprising that the trans isomer, analogous to $\phi = 180°$ of I, has a large positive J_{NN}^{Fc}, while the cis isomer, corresponding to $\phi = 0°$, has a large negative J_{NN}^{Fc} (unpublished calculations).
(15) The n_- molecular orbital depicted in VIa and VIb for $\phi = 0$ and 180°, respectively, may be thought of as arising from rehybridization of the π^* orbital of planar hydrazine on bending.

Resonance Energies of Benzenoid Hydrocarbons

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Abstract: Resonance energies for 48 totally benzenoid hydrocarbons have been calculated by means of HMO reference polynomials previously defined by us. In many respects they are fully consonant with SCF resonance energies calculated by Dewar and de Llano. Although our resonance energies are somewhat smaller than those of Hess and Schaad, there is an excellent linear relationship between the magnitudes of the two sets of resonance energies. Among the benzenoid hydrocarbons investigated, catacondensed hydrocarbons are predicted to be less stable than pericondensed hydrocarbons with a similar hue. A new definition of partial resonance energy, which describes aromaticity in individual π-electron rings, is proposed with the use of a Sachs formula and is justified in terms of Herndon's structure-resonance theory.

In previous papers,[1-3] we succeeded in defining an HMO characteristic polynomial for a nonaromatic "localized" structure of a conjugated compound by graph-theoretically excluding from the coefficients of an HMO characteristic polynomial of the compound all contributions from cyclic structures in the π system. This kind of polynomial was termed an HMO reference polynomial, because it is thought to give a reference energy, relative to which aromatic stabilization of the compound can be calculated. Most resonance energies calculated by Hess and Schaad[4-7] were analytically reproduced by means of such reference polynomials. On this basis, aromaticity in conjugated compounds can be safely attributed to the cyclic structures in the π system, in accord with our chemical sense that aromatic stabilization must be associated with π-electron rings.[8] We present here the application of this method to a wide variety of totally benzenoid hydrocarbons. The aromatic character in these compounds has been most extensively investigated by various methods.[1,2,4,5,9-14] Hence, we can take many viewpoints to examine our criterion of aromaticity. The HMO theory is assumed in its simplest form.

Calculation of A-II Resonance Energies. An HMO reference polynomial for a benzenoid hydrocarbon $R(X)$ can be expressed simply as[1]

$$R(X) = \sum_{k=0}^{N/2} (-1)^k p(2k) X^{N-2k} \qquad (1)$$

where N is the number of sp^2-carbon atoms in the π system, and $p(2k)$ is the number of ways in which k π bonds are so chosen from the π system that no two of them are connected to each other.[15] What we call the A-II resonance energy[1] is then defined as the difference between the total π energy calculated from a characteristic polynomial $P(X)$ of the com-