σ–π Parameters for the π Fragment C–CH–NH_2

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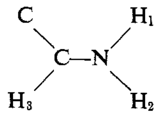
Abstract: σ–π polarization constants for the ^{14}N, ^{13}C, and H atoms in the π fragment $C–CH^3–NH^1H^2$ are calculated using the approach of Melchior, in which the set of interatomic σ bonds is orthonormalized. The following values for the polarization constants were obtained (G): $Q^{H_1}{}_{NN} = -24.3$, $Q^{H_2}{}_{NN} = -24.5$, $Q^{H_1}{}_{cross(CN)} = Q^{H_2}{}_{cross(CN)} = -3.2$, $Q^{H_3}{}_{CC} = -26.1$, $Q^{H_3}{}_{cross(CN)} = -2.6$, $Q^{H_3}{}_{NN} = -0.4$, $Q^{N}{}_{NN} = 19.4$, $Q^{N}{}_{cross(CN)} = 1.9$, $Q^{N}{}_{CC} = -5.0$, $Q^{C}{}_{CC} = 39.5$, $Q^{C}{}_{cross(CN)} = 3.0$, and $Q^{C}{}_{NN} = -11.5$. The main source of uncertainty in the calculations is the singlet–triplet excitation energies. The excitation energies $\sigma(C–H) \rightarrow \sigma^*(C–H)$ and $\sigma(C–H) \rightarrow \sigma^*(C–H')$ were estimated from a calculation of the σ–π parameters of the methyl radical for which the Q values $Q^{C}{}_{CC}$ and $Q^{H}{}_{CC}$ can be identified with the ^{13}C and H hyperfine coupling constants. A similar calculation on the NH_3^+ radical led to an estimation of the excitation energies $\sigma(N–H) \rightarrow \sigma^*(N–H)$ and $\sigma(N–H) \rightarrow \sigma^*(N–H')$. It was shown that the calculated elements of the Q matrix for the C–CH–NH_2 fragment are relatively insensitive to reasonable variations in almost all the remaining excitation energies. For purposes of comparison the Q matrix for the $N_2H_4^+$ ion was also calculated. The results do not seem to be compatible with a planar geometry for the radical. An attempt is made to rationalize the observed hyperfine splittings in the p-phenylenediamine cation radical using the Q values derived for the C–CH–NH_2 fragment.

Radicals derived from amino acids and peptides are of importance both chemically and in radiation biology. The interpretation of the esr spectra and the estimation of spin density distributions of such radicals are thus of considerable interest. In order to use observed hyperfine coupling constants (^1H, ^{13}C, ^{14}N) to derive spin-density distributions it is necessary to know the σ–π polarization constants of the radical (the Q matrix). In the present work we report a calculation of the elements of the Q matrix for the nitrogen, central carbon, and hydrogen atoms of the π fragment



The grouping C–C–NH_2 occurs in many amino acid radicals, where it carries almost all the unpaired spin. Moreover, the polarization constants are of wider application, since those for the nitrogen atom can be used in the interpretation of the spectra of amino radicals. The theoretical basis for the method used in the present work can be found in a recent paper by Melchior,[1] in which it is pointed out that previous calculations of polarization constants have given results which are over-sensitive to the model taken for the σ-bonding framework. Melchior demonstrates that this drawback is due to failure to orthonormalize the set of interatomic σ bonds. The values obtained for the polarization constants of the fragment treated in this work compare well with those estimated by other means for small related fragments. A point of particular interest is that the contribution to a_N of spin on the neighboring carbon atom is found to be negative and not negligible.

A theoretical study of isotropic hyperfine coupling constants of second-row elements in π radicals, based on unrestricted SCF–MO theory, has appeared very recently.[2] The σ–π parameters calculated for ^{13}C in the CHC_2' fragment and ^{14}N in the NC_2 fragment are in good agreement with those derived in this work.

Method of Calculation

The atomic orbital basis set used consisted of the carbon and nitrogen 1s, 2s, $2p_x$, and $2p_y$ orbitals and the hydrogen 1s orbitals. The carbon and nitrogen $2p_z$ orbitals are in the π system of the fragment. Slater orbitals were used with exponents for carbon and nitrogen being taken from Clementi and Raimondi.[3] For hydrogen 1s orbitals the exponent was taken as unity.

Interatomic distances (Å) were taken as C–C, 1.44; C–H, 1.08; C–N, 1.37; N–H, 1.03. The C–C and C–N distances were calculated by an SCF calculation as described by Nishimoto and Forster.[4] The N–H and C–H distances are typical values taken from the literature.[5] All interbond angles around carbon and nitrogen were taken as 120°.

The general computational framework is described fully by Melchior[1] and summarized extremely briefly in a paper by the present authors.[6] The σ-bonding and -antibonding system is constructed by Melchior's method and the resulting orbitals are used in the following expression to obtain the elements of the Q matrix for each atom considered. Equation 1 is taken

$$Q_{rs}{}^{N} = -(16/3)\pi g_N \beta_N \times \sum_i \sum_p \frac{\langle \sigma_i(p_z)_r | e^2/r_{12} | (p_z)_s \sigma_p{}^* \sigma_i(r_N) \sigma_p{}^*(r_N) \rangle}{[E(0) - E(i \rightarrow p)]} \quad (1)$$

from eq 26 of the paper by Henning[7] and was originally derived by McLachlan, Dearman, and Lefebvre[8] using slightly different nomenclature. To apply eq 1 it is necessary to evaluate the following quantities.

(1) Overlap Integrals. These enter into the process of constructing the orthogonalized σ-bonding systems. A program was written to evaluate overlap integrals using the general expression given by Roothaan.[9]

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(1) M. T. Melchior, *J. Chem. Phys.*, **50**, 511 (1969).

(2) T. Yonewaza, T. Kawamura, and H. Kato, *ibid.*, **50**, 3482 (1969).

(3) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

(4) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

(5) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **18** (1965).

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(7) J. C. M. Henning, *J. Chem. Phys.*, 44, 2139 (1966).

(8) A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *ibid.*, **33**, 65 (1960).

(9) C. C. J. Roothaan, *ibid.*, **19**, 1445 (1951).

(2) Exchange Integrals. One-, two-, three-, and four-center exchange integrals were computed using a program written in Autocode by Epstein[10] of this department.

(3) Singlet–Triplet Excitation Energies. The relevant excitation energies entering into eq 1 were estimated as follows.

(a) σ(C–H) → σ^*(C–H) and σ(C–H) → σ^*(C–H′). The Q matrix for the CH_3 group was calculated by Melchior's method, using Slater orbitals, and a CH bond length of 1.08 Å. The values of $Q^{H}{}_{CC}$ and $Q^{C}{}_{CC}$ are found to be given by the expressions

$$Q^{H}{}_{CC} = -27.3/A + 2.67/B$$

$$Q^{C}{}_{CC} = -10.4 + 23.7/A + 23.9/B$$

A is the intrabond (C–H) excitation energy and B the interbond excitation energy. Using "observed" values for $Q^{H}{}_{CC}$ and $Q^{H}{}_{CC}$ one can then solve the simultaneous equations to obtain A and B. The values taken for $Q^{H}{}_{CC}$ and $Q^{C}{}_{CC}$ were -24 and $+28$ G, respectively, which have been derived from studies of the temperature dependence and deuterium effect on the ^{13}C hyperfine splitting.[11,12] These values are estimated for CH_3 in the absence of vibrational distortion of the radical from planarity. We obtain $A = 1.06$ au and $B = 1.49$ au. As Melchior states, interbond excitation energies are expected to be larger than the corresponding intrabond excitations. The ratio obtained here for $R = A/B$ is 0.71. Melchior, in treating CH_2–CH_2^+, takes R between 0.5 and 1.0.

(b) σ(N–H) → σ^*(N–H) and σ(N–H) → σ^*(N–H′). In analogy to the calculation on CH_3, the Q matrix for NH_3^+ was derived and the inter- and intrabond excitation energies were obtained by using "observed" Q values. The N–H bond length was taken as 1.03. The results are

$$Q^{H}{}_{NN} = -29.2/A' + 3.42/B'$$

$$Q^{N}{}_{NN} = -4.69 + 12.76/A' + 12.38/B'$$

$Q^{H}{}_{NN}$ may be put equal to the observed proton hyperfine splitting constant[13] of -25.0 G in NH_3^+. Values of a^N of 18.0[13] and 19.5 G[14] have been reported for this radical. As in the case of CH_3 it is necessary to allow for the effect of vibrations on the central-atom splitting constant. In this connection it is of interest that for the $N(CH_3)_3^+$ radical, where the effect of vibration might be expected to be much smaller than for NH_3^+, a^N is 18.0 G.[15] Rather than attempt a lengthy, and possibly unreliable, estimate of vibrational effects, we have estimated the elements of the Q^N matrix taking values of a^N of 15 and 20 G. Using the above equations for $Q^{H}{}_{NN}$ we find for $a^N = 15$ G, $A' = 1.075$ au and $B' = 1.58$ au; and for $a^N = 20$ G, $A' = 1.03$ au and $B' = 1.01$ au. It is again worth noting that Melchior gives reasons for taking the ratio R of intrabond to interbond energies to be in the range 0.5–1.0. For this reason and because any vibrational correction to the observed a^N will reduce its value, we believe that the values of A' and B' calculated from $a^N = 15$ G are more acceptable. It is interesting that the values of A' are close to those estimated by direct calculation for the intrabond σ–σ^* excitations in C–C and C–O bonds.[6]

(c) Other Excitation Energies. In the treatment of the amino acid fragment considered here, many other excitation energies are needed, and these are enumerated later. It will be shown that the calculated elements of the Q matrix are usually relatively insensitive to any reasonable variation in these energies. This is fortunate, since they are not as readily estimated as the excitation energies for the C–H and N–H bonds. Excitation energies of the type 1s → σ^* were, as previously,[1,6,16] taken to be equal to the corresponding atomic X-ray term values.

We will apply Melchior's method, using the energies derived above, to an amino acid fragment. However, it is of interest to consider first a much simpler "test case," the $N_2H_4^+$ ion, for which experimental hyperfine splitting constants are available.[17]

The $N_2H_4^+$ Ion

The ion is at first assumed to be planar, and bond angles are all taken as 120°. The N–N bond length is put at 1.35 Å and the N–H bond length at 1.03 Å. The former bond length is a compromise between that in hydrazine[5] (1.47 Å), which is a pure σ bond, and values for conjugated N–N bonds (1.22–1.33) found in the literature.[5]

We define the following symbols for the excitation energies involved

A' = N–H σ bonding ⟶ N–H σ antibonding
B' = N–H σ bonding ⟶ N′H′ σ antibonding
C = N–N σ bonding ⟶ N–N σ antibonding
D = N—N σ bonding ⟶ N–H σ antibonding
E = N–H σ bonding ⟶ N–N σ antibonding

In terms of these energies we obtain

$$Q^{H}{}_{NN} = -29.5/A' + 1.85/B' + 0.9/D$$

$$Q^{H}{}_{cross} = -2.57/A' + 0.30/D$$

$$Q^{H}{}_{N'N'} = -0.25/A'$$

$$Q^{N}{}_{NN} = -4.88 + 9.1/A' + 4.46/B' + 4.61/C + 4.08/D + 5.16/E$$

$$Q^{N}{}_{cross} = 0.78/A' + 1.38/D$$

$$Q^{N}{}_{N'N'} = -0.33 - 4.61/C + 0.50/E$$

In writing the above expressions we have neglected some very small contributions from various interbond excitations. It can be seen immediately that the value of the proton hyperfine splitting constant is determined almost completely by the calculated values of A' and B'. The values of A' and B' will be taken from the treatment of NH_3^+ given above. The σ–σ^* excitation energy, C, for the N–N bond is taken as a parameter P, and all other interbond excitation energies are put equal to $P/0.75$. In Figure 1, the σ–π parameters for $N_2H_4^+$ are plotted as a function of P, for values ranging from 0.9 to 1.2 au.

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[11] R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
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[16] M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).
[17] J. Q. Adams and J. R. Thomas, *ibid.*, **39**, 1904 (1963).

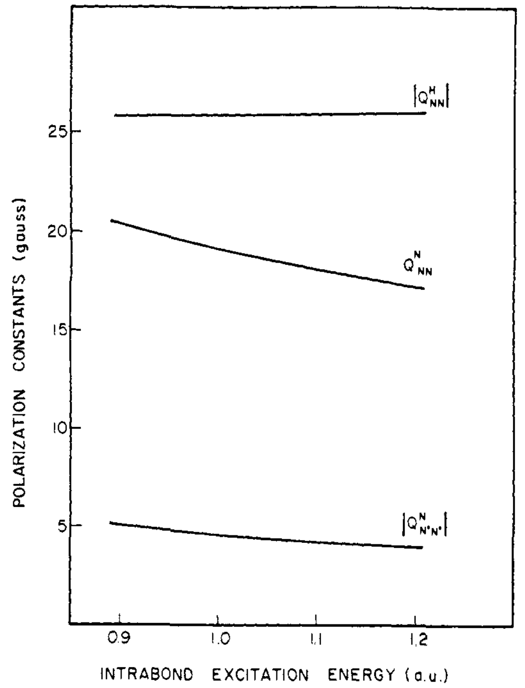

Figure 1. Polarization constants as a function of the intrabond excitation energy for the H_2N-NH_2^+ radical.

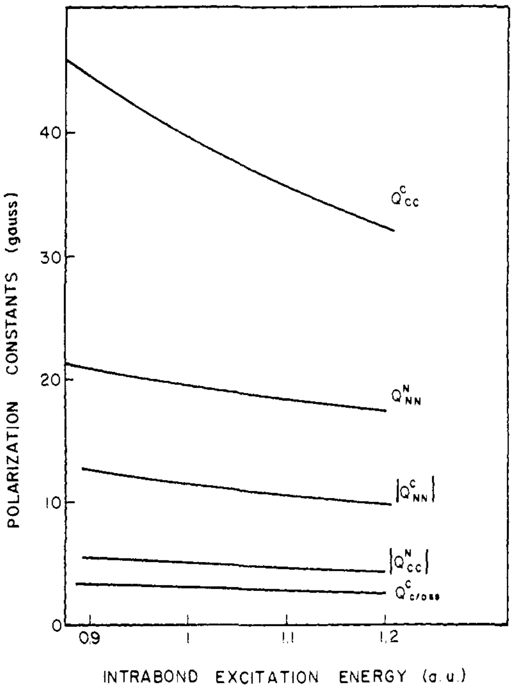

Figure 2. Polarization constants as a function of the intrabond excitation energy for the C–CH–NH_2 fragment.

A value of about 1.0 au for P is certainly reasonable when compared with theoretical calculations for bonds between first-row elements.[6] The value of 0.75 for R, the ratio of the intrabond to interbond excitation energies, is arbitrary, but acceptable in the light of the discussion of the calculations on CH_3 and NH_3^+. In any case the results for the Q matrix are affected only slightly by variations in R from 0.5 to 1.0. Using the two sets of A' and B' values obtained by taking a^N for NH_3^+ as 15 and 20 G, and putting $P = 1.0$ au we obtain the following σ–π parameters for planar $N_2H_4^+$ (G)

	For $a^N = 20$ G	For $a^N = 15$ G
Q^H_{NN}	−26.1	−25.6
Q^H_{cross}	−2.3	−2.2
$Q^H_{N'N'}$	−0.24	−0.23
Q^N_{NN}	19.9	18.0
Q^N_{cross}	1.79	1.76
$Q^N_{N'N'}$	−4.6	−4.6

The two sets of values for the Q^N matrix give, respectively, the following values (G) for the splitting constants in $N_2H_4^+$, taking $\rho_N = \rho_{N'} = 0.5$

a^N(calcd)	+6.75	+5.84
a^H(calcd)	−12.04	−11.8

compared with the experimental values of $|11.5|$ and $|11.0|$ G, respectively.[17] The discrepancy between experiment and theory can be largely removed if it is assumed that the radical is not planar, but rather pyramidal at each nitrogen atom: hydrazine itself has a dipole moment. We use the expression[11]

$$a^N(\theta) = a^N(0) + 550(2 \tan^2 \theta)\rho_N$$

where θ is the angle of the nitrogen $2p_z$ orbital to the direction it would have in the planar molecule. If we take the two calculated values of 6.75 and 5.84 G for $a^N(0)$ we derive $\theta = 5° 20'$ or $5° 50'$. Bending will introduce a small amount of positive spin density onto the hydrogen nuclei from the β nitrogen atom. This will reduce the calculated a^H. An estimate of this effect can be made by using the expression

$$a^H = B_0 + B_2 \cos^2 (90 - \phi)\rho_N$$

in analogy with the expression given for the protons of an NH_3^+ group β to a carbon atom.[18] For this case Whiffen and Collins[18] given $B_0 \simeq 0$ and $B_2 = 34$ G. Using these figures for the N–NH_2 group, we obtain "corrected" values of $a^H = -11.4$ or -10.9 G for the bent $N_2H_4^+$ radical. The calculated and observed hyperfine constants are thus in reasonable agreement if we assume that the $N_2H_4^+$ radical is not planar.

In putting $\rho_1 = \rho_2 = 0.5$, overlap has been neglected between the $2p_z$ orbitals on the nitrogens. Using the basis orbitals chosen here a value of 0.17 is obtained for the overlap, and corresponding values are found of $\rho_1 = \rho_2 = 0.606$. The splitting constants (G) calculated on this basis, using both sets of values for the Q^N matrix are

a^N(calcd)	+8.2	+7.1
a^H(calcd)	−14.6	−14.3

The bending angle θ derived from the two values of a^N is 4 and 4.6°, respectively, and the "corrected" values of a^H are -14.0 and -13.6 G, which are not in particularly good agreement with experiment.

Summing up the above analysis, it can be seen that any reasonable choice of excitation energies leaves a large gap between the observed a^N for $N_2H_4^+$ and a^N calculated for a planar radical. Note that the value of a^N(calcd) is completely independent of the value taken for A', the intrabond excitation energy.[19] Bending of the radical can account for the observed a^N, although it would obviously be advisable to have more data on related systems before accepting bending as

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[18] D. H. Whiffen and M. A. Collins, *Mol. Phys.*, **10**, 317 (1966).

[19] M. T. Melchior, private communication.

proved. In this connection the experimentally observed splitting constants in a number of other radicals containing the $-NH_2$ group can be rationalized in terms of bending angles close to those postulated for $N_2H_4^+$.[20]

Amino Acid Fragment

To evaluate the Q matrix for the amino acid fragment the following σ–σ^* excitation energies are needed

$$\mathrm{N{-}H} \longrightarrow \mathrm{N{-}H^*} = A' \qquad \mathrm{C{-}N} \longrightarrow \mathrm{C{-}C^*} = J$$

$$\mathrm{N{-}H} \longrightarrow \mathrm{N{-}H'^*} = B' \qquad \mathrm{C{-}N} \longrightarrow \mathrm{C{-}H^*} = K$$

$$\mathrm{C{-}H} \longrightarrow \mathrm{C{-}H^*} = A \qquad \mathrm{C{-}N} \longrightarrow \mathrm{N{-}H^*} = L$$

$$\mathrm{C{-}N} \longrightarrow \mathrm{C{-}N^*} = F \qquad \mathrm{N{-}H} \longrightarrow \mathrm{C{-}N^*} = M$$

$$\mathrm{C{-}C} \longrightarrow \mathrm{C{-}C^*} = G$$

$$\mathrm{C{-}C} \longrightarrow \mathrm{C{-}N^*} = H \qquad \mathrm{C{-}H} \longrightarrow \mathrm{C{-}N^*} = N$$

$$\mathrm{C{-}C} \longrightarrow \mathrm{C{-}H^*} = I \qquad \mathrm{C{-}H} \longrightarrow \mathrm{C{-}C^*} = R$$

In terms of the above energies we obtain the following values for the σ–π polarization parameters

$$Q^{H_1}{}_{NN} = -29.7/A' + 2.8/B' - 0.2/F + 1.0/L + 1.1/M$$

$$Q^{H_1}{}_{\mathrm{cross(CN)}} = -3.8/A' + 0.5L$$

$$Q^{H_1}{}_{CC} = -0.2/\mathrm{A}' + 0.2/F + 0.1/L$$

$$Q^{H_2}{}_{NN} = -29.9/A' + 2.8/B' - 0.2/F + 1.1/L + 1.0/M$$

$$Q^{H_2}{}_{\mathrm{cross(CN)}} = -3.9/A' + 0.6/L$$

$$Q^{H_2}{}_{CC} = -0.2/A' + 0.2F + 0.1/L$$

$$Q^{H_3}{}_{CC} = -28.8/A' + 0.1/F + 1.2/I - 1.1/N + 1.0/K + 0.3/R$$

$$Q^{H_3}{}_{\mathrm{cross(CN)}} = -2.8/A + 0.2/N - 0.1/K$$

$$Q^{H_3}{}_{NN} = -0.3/A - 0.2/K$$

$$Q^{N}{}_{NN} = -4.9 + 8.7/\mathrm{A}' + 4.2/B' + 5.5/F + 4.6/L + 4.7/M$$

$$Q^{N}{}_{\mathrm{cross(CN)}} = -0.2 + 1.1/A' - 0.4/F + 2.2/L - 0.3M$$

$$Q^{N}{}_{CC} = -0.35 - 5.0/F + 0.4/L$$

$$Q^{C}{}_{CC} = -12.6 + 9.0/A + 11.0/F + 8.5/G + 7.6/H + 4.7/I + 3.9/J + 3.9/K + 7.6N + 4.5/R$$

$$Q^{C}{}_{\mathrm{cross(CN)}} = -0.8 + 0.9/A + 0.8/F + 1.0/G + 0.6/H + 2.5/J - 0.2K - 1.3/N + 0.1/R$$

$$Q^{C}{}_{NN} = -1.1 - 12.1/F + 0.8/H + 1.1/J - 0.9/K + 0.4/R + 0.9/M$$

Of the formidable list of energies needed, A', B', and A have been discussed above, and we take $A' = 1.075$, $B' = 1.58$, and $A = 1.06$ au. The intrabond excitation energies F and G are taken equal and treated as a parameter (P). All the interbond excitation energies H–R are set equal to $P/0.75$. In fact the proton hyperfine splittings depend negligibly on the energies H–R. Apart from $Q^{C}{}_{CC}$, $Q^{N}{}_{NN}$, and $Q^{C}{}_{NN}$, the elements of the Q matrix are practically independent of P in the range 0.9–1.2 au.

If we again take the physically reasonable value of 1.0 au for P we obtain the following results (G)

$$Q^{H_1}{}_{NN} = -24.3 \qquad Q^{H_2}{}_{NN} = -24.5$$

$$Q^{H_1}{}_{\mathrm{cross(CN)}} = Q^{H_2}{}_{\mathrm{cross(CN)}} = -3.2$$

$$Q^{H_3}{}_{CC} = -26.1 \qquad Q^{H_3}{}_{\mathrm{cross(CN)}} = -2.6$$

$$Q^{H_3}{}_{NN} = -0.4$$

$$Q^{N}{}_{NN} = 19.4 \qquad Q^{C}{}_{CC} = 39.5$$

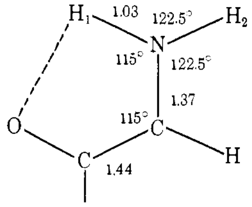
$$Q^{N}{}_{\mathrm{cross(CN)}} = 1.9 \qquad Q^{C}{}_{\mathrm{cross(CN)}} = 3.0$$

$$Q^{N}{}_{CC} = -5.0 \qquad Q^{C}{}_{NN} = -11.5$$

The above values for the σ–π polarization parameters are in very good agreement with the values expected from other theoretical and experimental studies. By way of comparison $Q^{H}{}_{NN}$ in aromatic amines has been previously estimated[21] as 26–28 G and in azines as 25–35 G. The value of $Q^{C}{}_{CC}$ is likewise in good agreement with the value of 37.8 G given by Melchior[1] for a related fragment. A very good estimate for $Q^{C}{}_{CC}$ can be obtained from the ^{13}C splitting of 45 G in the radical $CO_2^- \cdot CH{-}NH_3^+$,[22] assuming that all the spin is on one carbon atom.

The value of $Q^{N}{}_{NN}$ is slightly lower than that usually taken for nitrogen (*cf.* ref 2 for a compilation of nitrogen parameters). Of particular interest is the value of -5.0 G for $Q^{N}{}_{CC}$. Although Karplus and Fraenkel[16] and Henning[23] predict a negative sign for $Q^{N}{}_{CC}$ on theoretical grounds, Melchior has shown that positive and negative signs may occur for this type of matrix element if orthonormalization is imposed. Yonezawa, Kawamura, and Kato[2] give a value of -4.3 ± 0.8 G for $Q^{N}{}_{CC}$ in the fragment NC_2, and a value of $+1.3$ G for $Q^{N}{}_{\mathrm{cross(CN)}}$ compared with $+1.9$ G obtained here.

To account for the observed hyperfine splittings in amino acid radicals containing the fragment treated here, it is necessary to assume that the NH_2 group is not coplanar with the rest of the radical. A bending angle of 5–6° can account for the observed nitrogen hyperfine splittings in the radicals derived from glycine and α-alanine.[20] The nonequivalence of the two amine protons arose naturally from the calculation since their 1s orbitals have different overlap and exchange integrals with the rest of the radical. Such nonequivalence has been observed experimentally in a number of radicals.[20] In addition it might be expected that the carboxyl group would form a hydrogen bond with the amine group and thus tend to distort the radical. In order to estimate the magnitude of this



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[20] R. Poupko, A. Loewenstein, and B. L. Silver, *J. Amer. Chem. Soc.*, **93**, 580 (1971).

[21] G. Vincow, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 151.

[22] J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

[23] J. C. M. Henning, *Chem. Phys. Lett.*, **1**, 678 (1968).

effect the Q matrix was evaluated for such a model having the geometry shown in **1**. The results are

$$Q^{H_1}{}_{NN} = -28.7/A' + 2.6/B' + 1.1/M + 0.9/L$$

$$Q^{H_2}{}_{NN} = -31.5/A' + 3.1/B' + 1.2/M + 1.2/L$$

$$Q^{H}{}_{NN} = -4.7 + 9.0/A' + 4.3/B' + 4.4/M + 4.7/F + 4.1/L$$

Using the previous choice of energies we obtain

$$Q^{H_1}{}_{NN} = -23.6 \qquad Q^{H_2}{}_{NN} = -25.7$$

$$Q^{N}{}_{NN} = 18.6$$

This result should be taken as no more than an indication that the differences in observed amine–hydrogen splitting constants can be caused by quite modest distortions of the molecule.

Application to Aromatic Amines

The $\sigma-\pi$ parameters derived above can be applied to the esr spectra of aromatic amines. In *p*-phenylenediamine positive ion the ring proton splitting[24] $a^{H}{}_{ring} = 2.13$ G. Taking an effective value of -23 G for Q in McConnell's equation the spin density at each ring carbon atom is estimated to be 0.093. Thus if ρ_C is the spin density on the carbon atom bound to nitrogen we obtain $\rho_C + \rho_N = 0.314$. The expressions

$$a^{H}{}_{NH_2} = -24.5\rho_N - 3.2\rho_{CN}$$

$$a^{N} = 19.4\rho_N + 1.9\rho_{CN} - 5.0\rho_C$$

follow from the Q values calculated previously. If we take $\rho_C = 0.057$ and $\rho_N = 0.257$ we obtain $a^{H}{}_{NH_2} = 5.91$ G compared to 5.88 G observed experimentally. Using this value of ρ_N we obtain $a^N = 4.47$ G compared to the experimental value of 5.29 G. Once again the observed and experimental values for a^N and $a^{H}{}_{NH_2}$ can be accounted for if we allow the NH_2 group to be bent out of the plane of the aromatic ring. Taking $\theta = 3° 5'$ we derive $a^N = 5.29$ G and $a^{H}{}_{NH_2} = 5.88$ G, in agreement with experiment. The spin densities have been previously calculated to be $\rho_C{}^{(ring)} = 0.076$, $\rho_C{}^{(CN)} = 0.112$ and $\rho_N = 0.236$. A similar treatment of benzidine gave a bending angle of approximately 3° 30′. It is obviously not possible to base a proof of nonplanarity solely on this analysis of *p*-phenylenediamine and benzidene radicals, but the results suggest that a more thorough study of amine-radical hyperfine splittings could provide interesting information on their geometry.

Conclusion

The $\sigma-\pi$ parameters calculated in the present work generally agree well with those obtained for molecular fragments by other methods. The magnitudes of the different parameters are not sensitive to acceptable variations in most of the excitation energies, and most of the energies which are important can either be estimated by calculations on small radicals, or given values which are consistent with previous theoretical results. The $\sigma-\pi$ parameters for the amino group appear to be applicable to the hyperfine splittings observed in amines if bending of the NH_2 group is assumed. Such bending appears not only to be expected, but to occur in most radicals containing the $-NH_2$ group. The Q matrix calculated for the fragment considered in this work should be applicable to the esr spectra of any amino acid containing this fragment. Such an application, to radicals derived from glycine and α-alanine, is described in the accompanying paper.[20]

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(24) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).