Angular Dependence of the Electron-Acceptor Character of Alkylthio Groups in Organic Radicals

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Abstract: In the radical anions and nitroxides from p-alkylthionitrobenzenes, bulky alkylthiosubstituents produce a substantial decrease of the nitrogen hyperfine splitting, this being taken as an indication that they behave as π-electron acceptors. The temperature dependence of the coupling constant at the ^{13}C of the alkyl group directly bonded to the sulfur atom shows that these radicals experience progressive deviation from planarity with increasing size of the alkyl. The electron-acceptor character of the alkylthio group has therefore been explained in terms of electron transfer from the π orbital of the nitrobenzene moiety containing the unpaired electron to the σ^* vacant orbital of the S–R bond. INDO calculations, without the inclusion of the sulfur 3d orbitals, support such an interpretation.

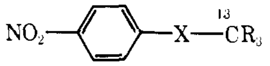
In a previous paper[2a] it was reported that, in the radical anions and nitroxides from alkylthionitrobenzenes, the alkylthio groups behave as electron-withdrawing substituents, their electron-acceptor character being greater the larger the size of the alkyl group. This behavior was tentatively explained in terms of σ–π conjugation which becomes increasingly important on passing from small-size SR substituents, which presumably are coplanar (or nearly so) with the aromatic ring, to bulky SR groups which are expected to adopt a conformation in which the alkyl sits above the molecular plane.

In the present paper we report experimental evidence confirming the predicted conformational preference of methylthio and *tert*-butylthio substituents, based on a detailed study of the temperature dependence of the hyperfine splitting constants at the ^{13}C attached to the sulfur atom. Values for the potential energy barriers to rotation of the alkyl groups have been determined. Experimental data obtained in a similar study on the radicals from the corresponding methoxy derivative are reported for comparison.

We report also the results of an INDO SCF MO investigation which has been carried out on the methylthio derivative. The effect of rotation on the electron spin density distribution and computed hyperfine splitting constants is discussed. In addition we have examined the implications of these results in connection with the problem of the electronic character of thio substituents in organic radicals.

Experimental Section

The ^{13}C enriched p-methoxynitrobenzene (I),[2b] p-methylthionitrobenzene (II),[3] and p-*tert*-butylthionitrobenzene (III)[3] were prepared according to methods described in the literature.



I, X = O; R = H
II, X = S; R = H
III, X = S; R = Me

$(CH_3)_3{}^{13}COH$, which was needed for the preparation of the latter sulfide, was obtained from the reaction of $CH_3{}^{13}COOCH_3$ with CH_3MgI.[4] The enriched $CH_3{}^{13}COOH$, $^{13}CH_3OH$, and $^{13}CH_3I$ were purchased from Stohler Isotope Chemicals.

The radical anions and nitroxides from I–III were generated as described previously.[2a] The sample temperature was measured with a copper–constantan thermocouple placed in the Dewar insert just above the sensitive part of the cavity.

Results and Discussion

The room temperature hyperfine splitting constants at the nitrogen and at the nuclei of the para substituent of the nitrobenzene anions and of the corresponding nitroxide adducts are reported in Table I. As it has been already pointed out[2a] the comparison of the a^N values for the substituted and unsubstituted radicals provides information about the overall electronic effect of the substituent. An increase of the nitrogen splitting after substitution suggests that the entering group has an electron-releasing character, while a decrease of the same constant is indicative of the electron-acceptor character of the substituent. An estimate of the separate σ and π contribution to the overall charge transfer can be obtained by examining the results for the related radicals substituted at the meta and para positions with the same group. In fact, the nitrogen splittings for the meta derivatives reflect mainly the effect of the σ-charge transfer since conjugative contributions should be negligible in these cases. Therefore the comparison with the values measured in the corresponding para radicals allows us to assess the direction and the extent of the π-charge transfer.

On these bases the experimental results (see Table I) provide the following information:

(1) In the meta derivatives a^N is always smaller than in the nitrobenzene anion or nitroxide, thus indicating that both the methoxy and the alkylthio substituents behave as σ acceptors, the effect being practically independent on the size of the alkyl group.

(2) The OCH_3 substituent acts as a good π donor in agreement with its well-known electron-releasing character.

(3) The π-charge effect of the SCH_3 group is negligible.

(4) The *tert*-butylthio group acts as a good π acceptor.

(5) The difference between the para SMe and S-*t*-Bu substituents cannot be due only to the different electronic effect of the methyl and *tert*-butyl groups since, when they are directly bonded to the phenyl ring, only negligible variations of the nitrogen splitting are observed (see Table I).

The unusual behavior of the alkylthio substituents may originate from a different degree of π conjugation between the aromatic ring and the SR group, if there is a change in the conformational preference of the R group by changing its size. A convenient way of determining the conformational stability of a XR substituent in π radicals is to measure the hyperfine splitting at the nucleus directly bonded to the X atom, because of the strong dependence of this coupling on the angle formed between the X–R bond and the nodal plane of the π system.[5]

Table I. Room Temperature Hyperfine Splitting Constants (G) of the Radical Anions (A) and Nitroxides (N) from Para and Meta (in Parentheses) Substituted Nitrobenzenes

substituent	radical	solvent	a^{N}	$a^{^{13}\mathrm{C}}$	$a^{\mathrm{H}}_{\mathrm{XR}}$
$O^{13}CH_3$	A	Me_2SO	11.05	0.44	0.31
	A	MeOH-DME	14.12 (12.86)	0.20	0.33
	N	Et_3SiH	15.82 (14.73)	<0.1	0.36
H	A	Me_2SO	9.89		3.94
	A	MeOH-DME	13.23		3.58
	N	Et_3SiH	14.86		3.19
$S^{13}CH_3$	A	Me_2SO	9.53 (9.53)	2.29	0.23
	A	MeOH-DME	12.86 (12.83)	1.34	0.34
	N	Et_3SiH	14.63 (14.66)	1.16	0.38
$S^{13}C(CH_3)_3$	A	Me_2SO	8.78 (9.61)	4.65	0.09
	A	MeOH-DME	12.27 (12.93)	3.62	<0.1
	N	Et_3SiH	14.03[a] (14.62)	2.83[a]	<0.1
CH_3	A	MeOH-DME	13.59		3.68
	N	Et_3SiH	15.12		3.34
t-Bu	A	MeOH-DME	13.60		<0.1
	N	Et_3SiH	15.06		<0.1

[a] $T = 10$ °C.

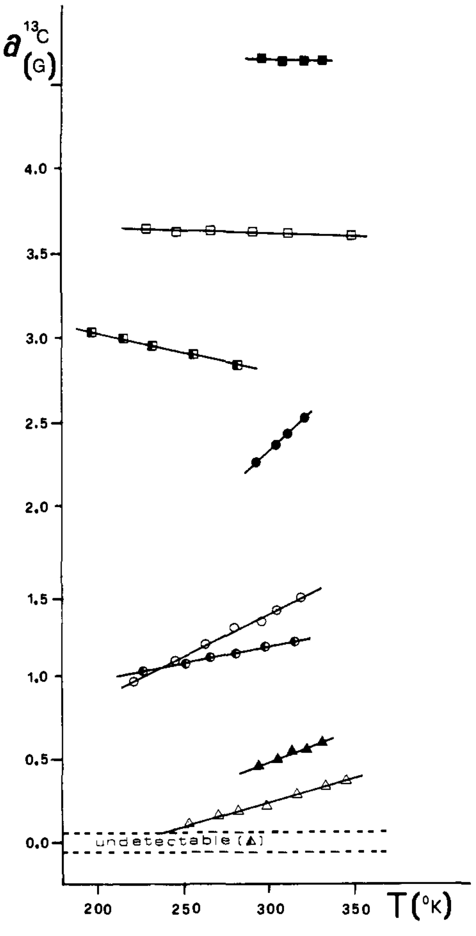
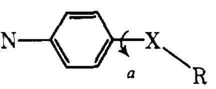


Figure 1. Temperature dependence of the ^{13}C hyperfine splitting constants in the radical anions (Me_2SO, full symbols; mixture 1:1:1 of MeOH, DME, and MeONa, empty symbols) and nitroxides (Et_3SiH, half-full symbols) from *p*-methoxy- (triangles), *p*-methylthio- (circles), and *p*-*tert*-butylthio- (squares) nitrobenzenes.

Since in both methylthio and *tert*-butylthio substituents this kind of information can be provided by the splitting at the carbon linked to the sulfur atom, we have prepared the ^{13}C-enriched compounds at this position.

The room temperature $a^{^{13}\mathrm{C}}$ hyperfine splittings measured in the radical anions and nitroxides from II and III are reported in Table I, together with the results for the analogous radicals from the ^{13}C-enriched *p*-methoxynitrobenzene, which were investigated for comparison. Figure 1 shows the temperature dependence of these splittings.

Conformational Analysis. INDO calculations, which will be described later in the paper, suggest that the functional dependence of the $a^{^{13}\mathrm{C}}$ constant of a carbon in this position in terms of the dihedral angle α formed by the plane of the aromatic ring and the plane containing the X-R bond and passing through the para carbon atom is described by eq 1. In all cases where the torsional energy levels are closely spaced, $\sin^2\alpha$ should be replaced by $\langle\sin^2\alpha\rangle$, that represents the ensemble average over the significantly populated levels.



$$a^{^{13}\mathrm{C}}(\alpha) = b_0 + b_2 \sin^2\alpha \quad (1)$$

Since in this case $b_0 \ll b_2$, as also found for β proton splittings,[5] we expect small values of the $a^{^{13}\mathrm{C}}$ constant when the XR substituent lies on the same plane of the aromatic ring, and large values when the molecule deviates significantly from planarity. An examination of Table I shows that the hyperfine splitting at the ^{13}C increases along the series OMe < SMe < S-*t*-Bu in both nitroxides and nitrobenzene anion radicals, thus suggesting that the α angle for the out-of-plane rotation of the R group increases in the same order.

More detailed information on the conformational behavior of these species can be obtained by studying the temperature dependence of the ^{13}C hyperfine splitting. If assuming a Boltzmann distribution over the torsional energy levels, $\langle\sin^2\alpha\rangle$ and therefore the value of $a^{^{13}\mathrm{C}}$ will increase or decrease with the temperature depending on whether the equilibrium conformation is the planar ($\alpha = 0$) or the orthogonal one ($\alpha = \pi/2$), respectively. The results of these measurements, which were made in different solvents, are reported in Figure 1. For the radical anion of the same substituted nitrobenzene, the values determined in Me_2SO are larger than in alcoholic solutions; these, in turn, exceed those measured in the corresponding nitroxide. Even the temperature dependence is considerably different in the various situations. However, from the similarity of the trends observed within the series of data concerning the same substituent, it can be deduced, on the basis of eq 1, that the average angle α should be very near to zero in the *p*-methoxy derivative, close to 90° for the bulky *tert*-butylthio group because $\mathrm{d}|a^{^{13}\mathrm{C}}|/\mathrm{d}T < 0$, and at some intermediate value in the case of the methylthio substituent.

Before proceeding to examine the way reliable estimates of the equilibrium position and barrier to internal rotation of the SR substituent may be obtained by analyzing the temperature dependence of the ^{13}C splitting,[6] we will briefly discuss the data of Figure 1, which provide a clear indication that also solvation effects are very important in determining the value of $a^{13\mathrm{C}}$, and that strongly solvating media (such as alcohols) favor a reduction of this coupling. The reasons for this behavior will be discussed in the following section; at present we must be aware that the temperature coefficient of the ^{13}C splitting might reflect, besides the variations of the Boltzmann distribution over the torsional levels, also changes in the solvation state of the radical. Actually we expect solvation, which is an exothermic process, to become more effective at lower temperatures. If this is the case, the absolute values of the measured positive or negative temperature coefficients will be misleadingly larger or smaller, respectively, than in the absence of solvation variations, since the latter process tends to produce a decrease of the ^{13}C splitting. The only way to overcome this impasse is to use a solvent with very weak solvating properties. This requirement is fulfilled by triethylsilane, and therefore a full analysis of the experimental variations of the ^{13}C splitting with temperature has been performed only in the case of the nitroxide adducts of the alkylthio derivatives II and III dissolved in the latter solvent. It should be pointed out that the addition of EtOH to Et_3SiH produces an increase of the temperature coefficient of $a^{13\mathrm{C}}$ in the case of the methylthio nitroxide and a flattening of the plot for the *tert*-butylthio nitroxide, in agreement with the above interpretation.

The experimental data may be analyzed by making use of eq 1, which accounts perfectly for the INDO calculated angular dependence of the ^{13}C hyperfine splitting constant. The computations show also that b_0 is very small when compared to b_2 and negative in the protonated radical. The ^{13}C splitting will therefore be a function of b_0, b_2, and the ensemble average $\langle \sin^2 \alpha \rangle$. If the first two parameters are known, $\langle \sin^2 \alpha \rangle$ may be determined at each temperature from the experimental coupling constant and then compared with the value calculated by choosing a particular form of the rotational potential. However, in the present case b_0 and b_2 are unknown and so we have developed a method for determining at the same time the two constants as well as the height of the rotational barriers in the two nitroxides from II and III.

By assuming that the internal rotation can be separated from the other degrees of freedom, the quantum mechanical treatment of this problem involves the determination of the eigenfunctions ψ_m and eigenvalues E_m of the pertinent Schrödinger equation[7]

$$-\frac{\hbar^2\delta^2}{2I\delta\alpha^2}\psi_m + V(\alpha)\psi_m = E_m\psi_m \qquad (2)$$

where I is the reduced moment of inertia for the rotation about the bond joining the para carbon and the sulfur atom. Given the large distance between the nitroxide function and the alkylthio substituent, the potential $V(\alpha)$ may be assumed to obey the symmetry conditions $V(\alpha) = V(-\alpha) = V(\pi \pm \alpha)$ and therefore can be expanded in even functions of the α angle, as

$$V(\alpha) = \frac{1}{2}\sum_k V_{2k}\,(1 + \cos 2k\alpha) \qquad (3)$$

By using as basis set the eigenfunctions of the free rotor, the normalized solutions of eq 2 may be separated into two sets, according to the parity inversion properties, as

$$\psi_m{}^{\mathrm{o}} = \sum_{\lambda=1}^{\infty} \frac{a_{m\lambda}}{\sqrt{\pi}} \sin 2\lambda\alpha \qquad (4)$$

$$\psi_m{}^{\mathrm{e}} = \frac{b_{m0}}{\sqrt{2\pi}} + \sum_{\lambda=1}^{\infty} \frac{b_{m\lambda}}{\sqrt{\pi}} \cos 2\lambda\alpha \qquad (5)$$

where $\psi_m{}^{\mathrm{o}}$ and $\psi_m{}^{\mathrm{e}}$ denote odd and even expansions, respectively. Giving numerical values to I and to the V_{2k} terms, the $a_{m\lambda}$ and $b_{m\lambda}$ coefficients may be calculated by diagonalizing the $\mathbf{H}^{\mathrm{o}}$ and $\mathbf{H}^{\mathrm{e}}$ matrices, whose elements are

$$H_{\lambda\lambda'}{}^{\mathrm{o}} = \left[\frac{2\hbar^2\lambda^2}{I} + \frac{1}{2}\sum_k V_{2k}\right]\delta_{\lambda\lambda'} + \frac{1}{2}V_{2(\lambda-\lambda')} - \frac{1}{4}V_{2(\lambda+\lambda')} \qquad (6)$$

$$H_{\lambda\lambda'}{}^{\mathrm{e}} = \left[\frac{2\hbar^2\lambda^2}{I} + \frac{1}{2}\sum_k V_{2k}\right]\delta_{\lambda\lambda'} + \frac{1}{4}V_{2(\lambda'-\lambda)} + \frac{1}{4}V_{2(\lambda'+\lambda)} \quad \text{for } \lambda' \geqslant \lambda \qquad (7)$$

$$H_{0\lambda'}{}^{\mathrm{e}} = \frac{1}{2}\sum_k V_{2k}\delta_{0\lambda'} + \frac{1}{\sqrt{8}}V_{2\lambda'} \qquad (8)$$

If the expansion is truncated to the nth term (in the present case $n = 50$ has been used), the expectation value of $\sin^2 \alpha$ in a given rotational state is

$$\langle\psi_m{}^{\mathrm{o}}|\sin^2\alpha|\psi_m{}^{\mathrm{o}}\rangle = \frac{1}{2} - \frac{1}{2}\sum_{\lambda=1}^{n-1} a_{m\lambda}a_{m\lambda+1} \qquad (9)$$

$$\langle\psi_m{}^{\mathrm{e}}|\sin^2\alpha|\psi_m{}^{\mathrm{e}}\rangle = \frac{1}{2} - \frac{1}{2}\left(\sqrt{2}b_{m0}b_{m1} + \sum_{\lambda=1}^{n-1} b_{m\lambda}b_{m\lambda+1}\right) \qquad (10)$$

and the ensemble average $\langle \sin^2 \alpha \rangle$ at a given temperature is

$$\langle\sin^2\alpha\rangle = \sum_m \langle\psi_m|\sin^2\alpha|\psi_m\rangle \times \exp(-E_m/kT) \Big/ \sum_m \exp(-E_m/kT) \qquad (11)$$

where the summations are carried out over the odd and even states.

In a first stage the computations have been made by truncating the expansion at the second term

$$V(\alpha) = V_0 + \frac{1}{2}V_2(1 + \cos 2\alpha) \qquad (12)$$

This potential simulates a single minimum at 0° by setting $V_2 < 0$, as it is in the case of the methylthio derivative (II), and a single minimum at 90° by choosing $V_2 > 0$, as required for the *tert*-butylthio radical from III. The choice of this kind of potential is justified in the case of II by the INDO results, while for III it is an assumption which will be discussed later on. The value of the reduced moment of inertia I was taken as 8.925×10^{-39} g cm^2 for the methylthio nitroxide and as 4.374×10^{-38} g cm^2 for the *tert*-butylthio analogue.

The following procedure has been adopted for determining b_0, b_2, and $|V_2|$. Since the experimental variations of the ^{13}C splitting are practically linear with temperature, the same should be true also for $\langle \sin^2 \alpha \rangle$, i.e.

$$\langle\sin^2\alpha\rangle = a_0 + a_2T \qquad (13)$$

or

$$a^{13\mathrm{C}} = b_0 + a_0b_2 + a_2b_2T = A + BT \qquad (14)$$

The constants A and B may be calculated from the experimental results, and a_0 and a_2 from the values of $\langle \sin^2 \alpha \rangle$ computed at different temperatures for given values of $|V_2|$. Equation 14 may then be used to compute the constants b_0 and b_2 which reproduce the experimental dependence of the ^{13}C splitting. Of course, for each derivative we have an infinite number of solutions for b_0 and b_2, as we may choose any arbitrary height of the rotational barrier. Since, however, these two parameters should be practically identical in the methylthio and *tert*-butylthio nitroxides, within the reasonable approximation that the spin density at the para carbon is the same

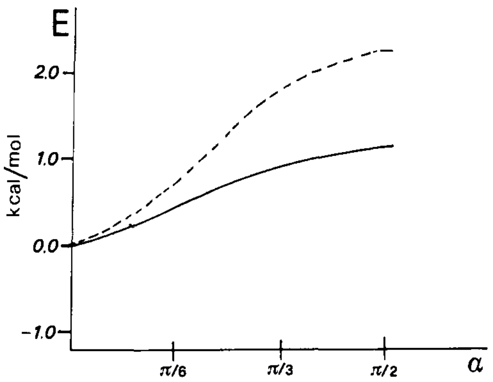


Figure 2. INDO computed potential energy for the rotation of the SCH_3 group in the unprotonated (solid line) and protonated (dashed line) anion radical of *p*-methylthionitrobenzene.

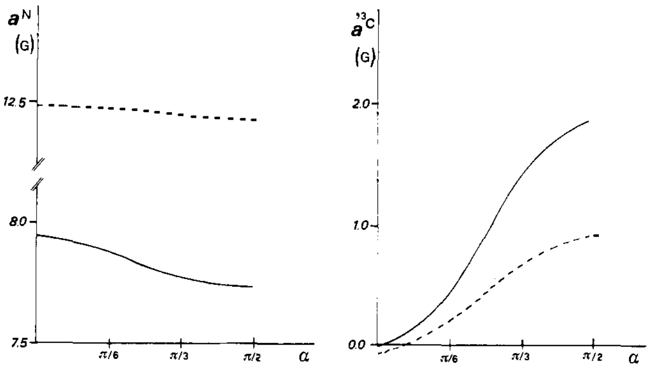


Figure 3. INDO computed angular dependence of the nitrogen and ^{13}C hyperfine splittings in the unprotonated (solid line) and protonated (dashed line) anion radical of *p*-methylthionitrobenzene.

in the two cases, the indeterminacy may be removed by choosing the values of b_0 and b_2 satisfying this condition. To show the sensitivity of the method, in Figure 5 are reported the plots of b_0 against b_2 for the two nitroxide adducts. The crossing point provides the values of b_0 and b_2 as −0.03 and 3.45 G, and of the heights of the rotational barriers as 0.77 and 2.03 kcal/mol for II and III, respectively.

It should be pointed out that the b_0 constant determined in this way is in good agreement with the INDO calculations which predict b_0 to be much smaller than b_2 and negative. This gives us some confidence on the reliability of the assumed potentials with a single minimum at 0 and 90° for II and III, respectively. Actually in a second stage attempts to reproduce the temperature dependence of the ^{13}C splitting were also made by using double minimum potentials or by shifting the single minimum at some angle intermediate between 0 and 90°. This has been done by retaining in eq 3, which gives the form of the potential, higher order terms and repeating the calculations. Since in all cases the computed b_0 and b_2 constants were completely out of any reasonable range, alternative possibilities for the potential can be rejected in favor of those giving a single minimum at 0 or 90°.

By knowing b_0 and b_2, eq 1 can now be used to determine the value of $\langle \sin^2 \alpha \rangle$. At room temperature this average is 0.34 for the methylthio nitroxide from II and 0.82 for the butylthio nitroxide from III. These values indicate that both the alkylthio substituents, on the average, deviate significantly from planarity, the out-of-plane angle being much larger for the *tert*-butyl group.

In the case of the methoxy derivative I, the same procedure leads to the conclusion that α is very small, with the assumption that b_0 and b_2 for the $O\text{-}^{13}CR_3$ and $S\text{-}^{13}CR_3$ groups are not too different.

INDO Calculations. The analysis of the temperature dependence of the ^{13}C hyperfine splittings seems to provide some support to the interpretation that the different electronic behavior of the methylthio and *tert*-butylthio substituents originates from a change in the extent of π conjugation due to their different spatial arrangement.

With the purpose to obtain a better understanding of the real nature of these effects we have carried out INDO SCF MO calculations on the radical anion of *p*-methylthionitrobenzene (II), at various values of the angle α for the rotation of the SMe group. The program was parametrized for second-row elements according to Benson and Hudson,[8] and no sulfur 3d orbitals were included in the computations. For the phenyl ring we have used a standard hexagonal geometry, while the other parameters have been optimized for the planar conformation and kept fixed during rotation. The optimized bond distances and bond angles follow: C–N = 1.40 Å, N–O ≈ 1.27 Å, ∠ONO = 120°, C(Ph)–S = 1.83 Å, S–C(Me) = 1.814 Å, ∠C(Ph)SC(Me) = 107°. In order to take into account the effect of solvent on the rotational barrier and hfs constants, the alcohol solvated radical, in which hydrogen bonding to the oxygen atoms occurs, was described by protonating the NO_2 group.[9] The proton was placed on the C_{2v} symmetry axis of the nitro group at a distance of 1.3 Å from the oxygens, and the other geometrical parameters were left unchanged. This limiting case represents also a reasonable model for the nitroxide radical for which computations were not performed. The results of these calculations are summarized in Figures 2 and 3, which report the potential energy curve for rotation and the variations with α of the nitrogen and ^{13}C hfs constants of the protonated and unprotonated radical anion of II. From Figure 2 it appears that, in both cases, the radical is more stable in the planar conformation, the energy differences with respect to the orthogonal conformation being 1.09 and 2.25 kcal/mol in the unprotonated and protonated anion, respectively. Furthermore, the hfs constants show a pronounced angular dependence, which is larger in the unprotonated radical.

This behavior can be satisfactorily rationalized in terms of a one-electron MO (OEMO) analysis, focusing upon the more important interactions involving the relevant MOs of the nitrobenzene fragment and those of the SCH_3 substituent in the planar and orthogonal conformations. The pertinent interaction diagram is shown in Figure 4. In the planar conformation the important interactions are those occurring between the sulfur lone pair of π type ($n_S{}^\pi$) and the LUMO (lowest unoccupied MO) of the negative nitrobenzene fragment that lies at very low energy, while in the orthogonal conformation those occurring between the SOMO (singly occupied MO) of the nitrobenzene anion and the vacant low-lying σ^* MO orbital associated with the S–Me bond. Both interactions are stabilizing; however, while the $n_S{}^\pi$ LUMO causes a charge transfer from the substituent to the $[NO_2\text{-}C_6H_4]^-$ fragment, the SOMO $\sigma^*{}_{S\text{-}C}$ causes a charge transfer in the opposite direction.

Protonation has the effect of decreasing much more the energy of the MOs of the nitrobenzene moiety than those of the SCH_3 group, that to a first approximation can be kept unchanged. Therefore protonation will reduce the energy gap between the $n_S{}^\pi$ and the LUMO with consequent additional stabilization of the planar conformation, and will make larger the energy gap between the SOMO and the $\sigma^*{}_{S\text{-}C}$ bond MO, causing a decrease in the stabilization of the orthogonal conformation. The sum of the two effects produces the increase of the potential energy barrier to the rotation of the methyl group which results from the INDO computations.

This interpretation is also consistent with the reduction, after protonation, of the electron transfer from the SOMO to the σ^* vacant orbital of the S–Me bond indicated by the decrease of the ^{13}C hyperfine splitting in the perpendicular structure.

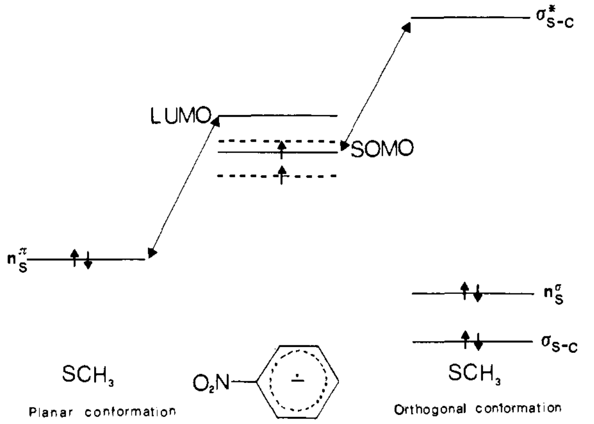


Figure 4. Interaction diagram between the singly occupied (SOMO) and first vacant (LUMO) molecular orbitals of the $[NO_2\text{-}C_6H_4]^{-}\cdot$ fragment, and the lone pair and σ MOs of the SMe substituent. The dashed line refers to the protonated radical.

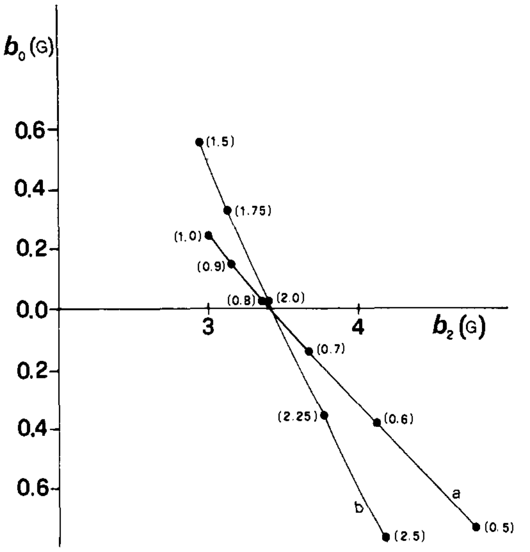


Figure 5. Plot of b_0 against b_2 (see eq 1) optimized to give the best agreement with the experimental temperature dependence of the ^{13}C splitting for given values of the rotational barrier (reported in parentheses) in the nitroxide adducts of the (a) *p*-methylthio- and (b) *p*-*tert*-butylthionitrobenzenes.

The angular dependence of the computed nitrogen coupling may be explained on a similar basis, since its decrease on going from the planar to the orthogonal conformation can be related with the increasing extent of the electron transfer from the π system to the carbon-sulfur bond, which is larger in the unprotonated anion radical.

The INDO calculations and OEMO analysis give a satisfactory explanation of the experimental results. Actually if the average rotation angle α of the S-R bond is much greater in the *tert*-butylthio- than in the methylthionitrobenzene, as discussed previously, the larger splitting at the ^{13}C and the smaller value of a^N measured in the former derivative are qualitatively consistent with the calculated angular dependence of these constants. Therefore the interpretation that the electron-acceptor character of bulky alkylthio substituents is due to electron release from the π system to the σ^* MO of the S-R bond is strongly substantiated by the present results. Similar considerations will also explain the large withdrawing effect of PhS and PhSe groups observed in para-substituted 1-phenyl-1,2-propanesemidiones,[10] which was previously attributed to participation of the sulfur or selenium d orbitals in the π bonding.

Also the solvent dependence of the ^{13}C hyperfine splitting is nicely accounted for by our INDO calculations and OEMO analysis. It should be noticed that spin density variations at the para position, which might in principle produce the same effect, are considerably smaller as they result from the values of the para-proton splitting for the unsubstituted derivative measured in different solvents (see Table I).

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