Solvation of Organic Oxyanions Studied by ^{17}O NMR

Lars Baltzer*† and Edwin D. Becker

Contribution from the Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20205. Received November 10, 1982

Abstract: ^{17}O NMR line widths have been measured for the 4-nitrophenolate anion, 4-nitroanisole, the benzoate anion, and methyl benzoate in methanol, dimethyl sulfoxide, and mixtures of the two solvents. For the compounds in the given order the line widths vary between 545 and 844 Hz, 271 and 817 Hz, 368 and 498 Hz, and 155 and 467 Hz. The Me$_2$SO solutions generally give the widest lines. The relaxation rates of the neutral compounds vary linearly with the solvent viscosity whereas those of the anions are more complex. The results are interpreted in terms of desolvation of the anion by Me$_2$SO.

The elusive properties of the solvent shell surrounding solute species have been studied in many different contexts and with a variety of methods.[1] Our particular interest lies in the solute–solvent interactions between the organic oxyanions and hydroxylic/dipolar nonhydroxylic solvents. In the present investigation the anions are studied in solvents where they exhibit considerable and regular changes in basicity and reactivity as a function of solvent composition.[2] The method used here focuses on the immediate environment of the charged atom since it has been shown in the case of alkali and halide ions that changes in the solvation energy are to a good approximation to be found in the interactions between the ion and the first solvation shell surrounding it.[3] In a previous study[4] it was concluded from isotope effects on proton chemical shifts that the methoxide ion in mixtures of methanol and Me$_2$SO was partly desolvated at low mole fractions of the latter solvent. A kinetic study of the racemization of optically active biphenyl derivatives in these and other solvents[5] gave evidence that biphenolates are also partly desolvated at rather low mole fractions of Me$_2$SO in mixtures of Me$_2$SO and hydroxylic solvents. That is a somewhat surprising result, particularly in view of the strong basicity of oxyanions. Hence, we were interested in finding a probe for gaining more information about the structure of the first solvation sphere of oxyanions and for confirming the earlier results in an independent investigation.

Interactions between solute and solvent are suitably studied by NMR techniques. It is especially tempting to use a nucleus that is directly involved in the interaction. With cations this approach has been extensively used.[1,6–9] but in spite of the importance of organic oxyanions, ^{17}O NMR has not to our knowledge been used for that purpose. The low natural abundance (0.037%) and relatively high cost of enriched material may appear discouraging, but its sensitivity is twice as high as that of ^{13}C and the synthesis of enriched material is in many cases trivial. From an NMR spectroscopist's point of view the advantage is that due to its quadrupole moment ($I = {}^5/_2$, $eQ = 2.6 \times 10^{-2}$ barns) the oxygen relaxes in the millisecond range. Consequently, one may pulse rapidly, and several hundred thousand scans may be collected in less time than it takes to collect a good natural abundance ^{13}C NMR spectrum in a sample of comparable concentration. Although it is true in many instances that ^{13}C NMR promotes easier access to information also obtainable by ^{17}O, e.g., using ^{18}O/^{16}O isotope effects,[10] it will be clear from the present investigation that the latter method is better for probing motional anisotropy of organic oxyanions. For a general reference to ^{17}O NMR see ref 11.

Experimental Section

The compounds used were synthesized and purified by using standard procedures. 4-Nitro[^{17}O]phenol was prepared by nucleophilic substitution of 4-nitroiodobenzene in a mixture of Me$_2$SO and enriched water containing sodium hydroxide. Its lithium salt was prepared by dissolving excess phenol in methanol containing lithium hydroxide followed by

evaporation of the solvent and thorough washing of the crystals with diethyl ether. 4-Nitroanisole was prepared from the phenol and dimethyl sulfate by using a phase-transfer catalysis technique.[12]

[^{17}O]Benzoic acid was prepared by alkaline hydrolysis of methyl benzoate in aqueous acetone containing H$_2$^{17}O. Its potassium salt was precipitated from methanol by addition of chloroform.

Methyl [^{17}O]benzoate enriched in the methoxylic position was synthesized from enriched methanol and benzoyl chloride in benzene containing pyridine. The ^{17}O NMR spectrum confirms the position of the enrichment. The methanol was obtained from trimethyl phosphate and H$_2$^{17}O.[13] The ^{17}O enrichment in the compounds used varies between 10 and 20%.

Solutions for NMR of the lithium salt of I contained a complexing agent, 12-crown-4, to avoid ion pairing when the solvent was methanol or 25 mol % Me$_2$SO in methanol. In the latter solvent the effect of the complexing agent was negligible and no crown ether was added to the other solutions.

Methanol-d_4, 99.5% D. Merck & Co., was used without further purification. Me$_2$SO-d_6, 99.5% D. Merck & Co., was stored under dry argon over freshly baked molecular sieves, Linde type 4A pellets, and used without further purification. Methanol without deuterium was sometimes used in solutions of high Me$_2$SO content. It was refluxed for several hours over magnesium turnings and fractionally distilled under an atmosphere of dry argon and stored over freshly baked molecular sieves.[14]

NMR measurements were performed at 36.61 MHz on an NIH-modified spectrometer equipped with a superconducting Bruker magnet and a Nicolet 1180 computer system. A 90° pulse was 78 μs, and in a typical run the acquisition time was 5–10 ms and the sweep width 24 000

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†Present address: Department of Organic Chemistry, University of Göteborg and Chalmers University of Technology, S-412 96, Göteborg, Sweden.

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Hz. (Parameter optimization for the solutes gives an acquisition time of 2.5 ms, but the acquisition times chosen were the shortest ones possible to avoid spectrum distortion by the narrower solvent resonances.[15]) The pulse repetition time was usually a few milliseconds longer than the acquisition time. The memory was zero filled up to 2K data points before FT. The acquisition delay time was between 100 and 250 μs and was equal to the reciprocal of the shift between the compound peak and the closest solvent peak to simplify phase corrections before line fitting.[16] No exponential filter was used. Line widths were determined by fitting a Lorentzian expression to the experimental data. No decoupling was used to avoid heating of the samples, and therefore a slight broadening of the lines with II and IV may occur because of coupling with the methyl groups. The coupling constant may be taken as small (that of $^2J_{OH}$ in methyl formate has been reported as 7.5 Hz[17]) and certainly constant throughout the series of solvents used. Ample time was allowed for temperature equilibration of the samples and the temperature was checked on several of the samples. A glass-encapsulated thermocouple was inserted into the NMR tube immediately after it was ejected from the magnet. Less than 20 s elapsed, and the temperature was found to be very steady with deviations from 31 °C of 1 °C or less.

Results and Discussion

The objective of the present investigation is to learn more about the solvation shell around the charged oxygen atom in some moderately basic oxyanions. The particular problem under investigation concerns the change in the solvation shell in methanol solution when the methanol is gradually displaced by Me_2SO. Addition of Me_2SO to hydroxylic solvents increases reactivity and basicity of organic oxyanions, but in spite of the many years since that discovery[18] a detailed explanation for this behavior is still lacking. Different factors have been identified as contributing, desolvation of the anion by Me_2SO and increased solvation of the corresponding acid by Me_2SO being two of the more important.[1a] For information to be obtained about the relative importance of anion desolvation, the molecular structure of the solvation shell has to be known in some detail. Previously, kinetic measurements[4,19,20] and isotope effects on chemical shifts[3] have been used to study some model systems in hydroxylic solvents and mixtures with Me_2SO. It was concluded that the strongly basic methoxide ion was partly desolvated already at low mole fractions of Me_2SO in methanol Me_2SO mixtures.[3] At 60 mol % Me_2SO the dominant species in solution is the methoxide ion hydrogen bonded to two methanol molecules, as compared with three in pure methanol. This may appear surprising since hydrogen bonds to the methoxide ion are expected to be strong in these media and a reasonable guess would have been that the methoxide ion should have been completely solvated even at very high mole fractions of Me_2SO. The explanation was given that the hydrogen-bond strength between methanol and the methoxide ion increases in the order MeO⁻(MeOH)₃ < MeO⁻(MeOH)₂ < MeO⁻(MeOH). In order to gain more hard evidence for this theory and also to study its applicability to bases of other types and less basicity, we undertook the present study, using ^{17}O NMR. The experimental results are in Table I. The approach is based on the fact that the relaxation rate, R, is related to molecular motion and consequently the size of the complex containing the resonating nucleus. Since relaxation of ^{17}O is dominated by nuclear quadrupole interactions, the relation is particularly simple.

$$R = 1/T_1 = 1/T_2 = (3/125)(e^2Qq/h)^2\tau_c \qquad (1)$$

In eq 1, which may be found in most elementary textbooks, T_1 and T_2 are the spin–lattice and spin–spin relaxation times, re-

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Table I

compd	solv[a,b]	line width,[c] Hz	δ^d
I	M	570	210
	25D–75M	545	231
	50D–50M	598	255
	75D–25M	645	285
	D	844	318
II	M	271	69
	25D–75M	356	67
	50D–50M	499	68
	75D–25M	603	70
	D	817	72
III	M	368	262
	25D–75M	390	266
	50D–50M	454	269
	75D–25M	498	272
	D	484	281
IV	M	155	131
	25D–75M	221	131
	50D–50M	293	130
	75D–25M	378	131
	D	467	130

[a] D = dimethyl-d_6 sulfoxide, M = methanol-d_4 or methanol-h_4 (see Experimental Section). [b] Temperature is 304 K. [c] Error limits in line widths are believed to be less than ±5%. [d] Chemical shifts are relative to D_2O (99.7%, Merck Isotopes) and are believed to be ±1 ppm.

spectively, Q is the nuclear quadrupole moment, q is the electric field gradient, and τ_c is the correlation time. The expression within parenthesis is the nuclear quadrupolar coupling constant (NQCC). The equation assumes extreme narrowing conditions and is strictly applicable only to a molecule in which the electric field gradient has axial symmetry and the molecular tumbling is characterized by a single correlation time. Approximately axial symmetry occurs about the C–O bond, and the assumption of a single τ_c is reasonably good for the systems studied here. The correlation time contains information about the effective size of the "cluster" under study. Determination of the line width, $\Delta\nu_{1/2}$, is a convenient way of obtaining relaxation data, since $\Delta\nu_{1/2} = 1/\pi T_2$.

Let us briefly outline what kind of complexes one expects in the different solvents and how they may be detected by ^{17}O NMR.

Oxyanions that do not have substituents close enough to the oxygen atom to perturb the hydrogen-bonded solvent molecules are expected to form complexes in hydroxylic solvents, like methanol, where three solvent molecules are bound to each charged oxygen. This is quite reasonable since there are three electron pairs available for hydrogen-bond formation. Strong support in the case of the methoxide ion comes from kinetic solvent isotope effects in connection with fractionation factor measurements of the methoxide ion in methanol.[21] Because of the special structure of the carboxylate anion where an electron pair is delocalized over three atoms, four electron pairs may be considered available for hydrogen bonding to solvent molecles but no evidence exists, as far as we know, about this question.

In Me_2SO, which is not a hydrogen-bond donor, there are no solvent molecules complexed with the anion and consequently the tumbling moiety is much smaller than that in methanol. Since rapid tumbling corresponds to a short correlation time, the lines should, neglecting so far all other factors, be narrower in Me_2SO than in methanol. The line widths in mixtures of intermediate Me_2SO content will tell us to what degree the desolvation progresses. Two limiting cases may be outlined: If the anion is partly desolvated at low mole fractions of Me_2SO the line width would be expected to approach that in Me_2SO very quickly as Me_2SO is added to methanol. If the opposite is true, however, the lines would be expected to be essentially constant until very high mole fractions of Me_2SO where a sharp change should occur. The expression "partial desolvation" is used to demonstrate that desolvation is a stepwise process, as expected for statistical reasons. Me_2SO may desolvate more efficiently than would be expected

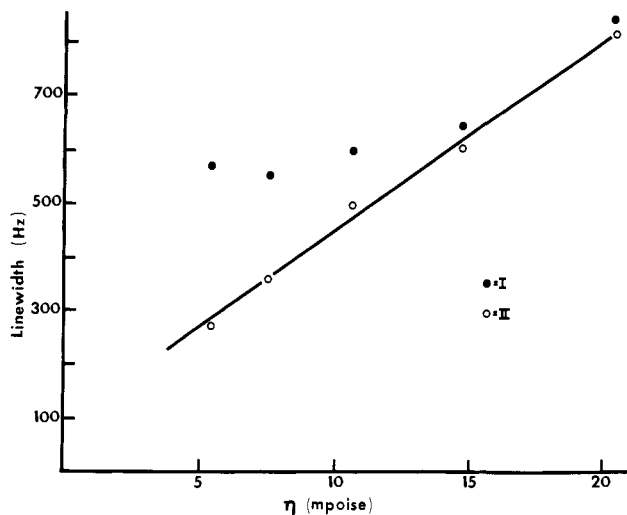(21) Gold, V.; Grist, S. *J. Chem. Soc. B* **1971**, 2282–2285.

Figure 1. Oxygen-17 line widths of I and II vs. viscosity of the solvent ($T = 304$ K). The line width of II is a linear function of the viscosity, and a least-squares fit of the data gives a slope of 35.8 and an intercept of 86 (viscosity data from ref 27).
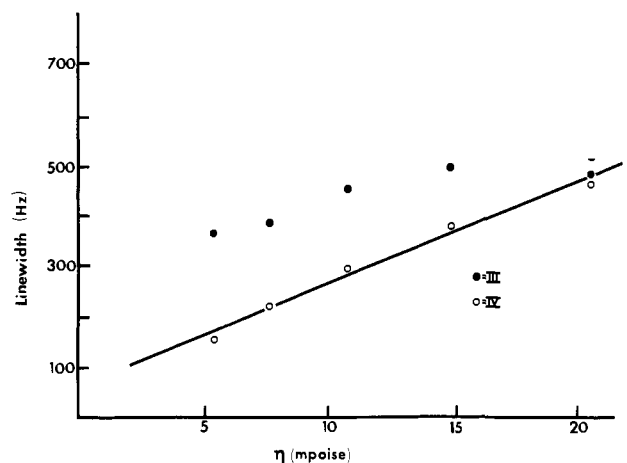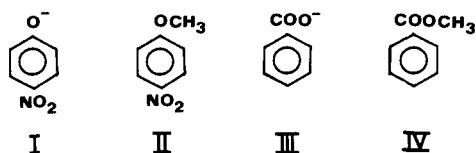

Figure 2. Line widths of III and IV vs. viscosity of the solvent ($T = 304$ K). A least-squares fit of the data for IV gives a slope of 20.5 and an intercept of 61 (viscosity data from ref 27).

on such grounds and should not be looked upon as an inert solvent exercising a dilution effect. Since Me_2SO is a very viscous solvent ($\eta = 19.8$ mP, 298 K), it is essential to measure $\Delta\nu_{1/2}$ relative to some model compound that does not form hydrogen bonds to the solvent to any appreciable degree. The relaxation of the model compound would then not reflect specific solute–solvent interactions but only the change in viscosity. Solvent effects on relaxation by viscosity may otherwise be mistaken for increased solvation.

The relaxation data for the 4-nitrophenolate anion (I) and 4-nitroanisole (II) are given in Figure 1, those of the benzoate anion (III) and methyl benzoate (IV) in Figure 2, and the cor-

responding relaxation rate ratios R_I/R_{II} and R_{III}/R_{IV} in Figure 3. In Figure 3 are also included curves qualitatively giving the expected behavior for the two limiting cases as outlined above. The relation between line widths does not have an obvious quantitative interpretation. The NQCCs are complex and will be discussed later. Several correlation times exist for each molecule when anisotropic motion prevails. In order to find a simple physical picture describing the relaxation, assumptions have to
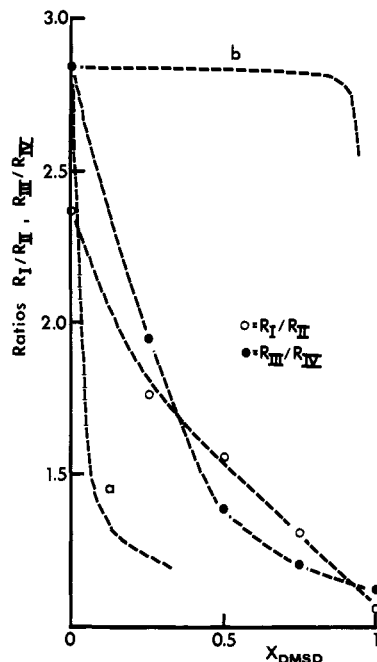

Figure 3. Ratios of relaxation rates vs. mole fraction of Me_2SO ($T = 304$ K). The dotted lines a and b represent extreme cases of "immediate" desolvation and "late" desolvation; see text.

be made. If I–IV may be taken as being axially symmetric around an axis through carbons 1 and 4 of the aromatic ring, the relaxation rate is governed only by the diffusion around the two axes perpendicular to the symmetry axis in the following way[22]

$$1/T_1 = 1/T_2 = (3/125)(NQCC)^2(1/6D) \qquad (2)$$

where D is the rotational diffusion constant. In this simplified case the change in the ratio of line widths with change in solvent simply reflects the change in tumbling rate between the anion and its homologue. Although too crude to permit any calculations of cluster size, the physical picture conveyed by this model probably gives a very good description of the actual desolvation process. It is at this point too early to attempt a molecular picture in terms of different complexes at different compositions, but it is clear from the data that the desolvation process is well under way already at low mole fractions of Me_2SO for both I and II.

Although the molecular dimensions of I and II are very similar as are those of III and IV, the differences in relaxation rate in methanol are striking. In Me_2SO, however, they are very much the same. The relaxation rates of the anions rapidly approach those of the neutral compounds with an increase in mole fraction of Me_2SO and the ratios R_I/R_{II} and R_{III}/R_{IV} are much closer to curve a than to curve b in Figure 3. The similarity of relaxation rates within the pairs in Me_2SO is strongly supportive of the assumption that II and IV serve as good models for "naked" I and III, respectively. Also, the linear dependence on viscosity over this range for II and IV is predicted for solutes without strong interactions with the solvent, the difference in slope between them being attributable to the difference in size. A detailed explanation for the course of curve I, Figure 1, is somewhat speculative, but it may well be a composite of two effects counteracting each other. The desolvation process tends to sharpen the line whereas the increased viscosity has the opposite effect. (For a discussion of the effect of a change in NQCC see below.) Curve III, Figure 2, is more difficult to explain on the basis of a two-parameter model since the line width is at best constant from 75 to 100 mol % Me_2SO with maybe even a tendency to decrease. The possiblity that III should be completely desolvated in 75 mol % Me_2SO is ruled out by the fact that there is a difference between III and IV in this solvent. Instead, it is conceivable that rotation of the carboxylate moiety around the symmetry axis may contribute to

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relaxation, less in DMSO than in methanol because hydrogen bonding decreases the rate of rotation in the latter solvent.

Inherent so far in this treatment is the assumption that the ratios of NQCCs is constant between the anions and the corresponding models throughout the range of solvents and that the ratios in Figure 3 reflect ratios of correlation times. The validity of such a supposition is not self-evident. The NQCC is expected to change with charge density on the oxygen nucleus. From ^{17}O chemical shifts, Table I, as well as the effect of the nitro group in interacting with negative charges close to the aromatic ring in analogous compounds,[23] it is clear that a substantial change is in fact taking place on the charged oxygen in I, with charge density going into the ring giving more double-bond character to the C–O bond. To our knowledge no NQCC data exist on such a system, but from reports on solids an order-of-magnitude estimate may be obtained. The NQCC of sodium formate (SF) has been reported as 7.311 MHz[24] and that of potassium hydrogen diformate (PHDF) as 5.644 MHz.[25] In SF both oxygens are equivalent, but in PHDF, a strongly hydrogen-bonded system, the C–O bond directly involved in the hydrogen bond has more single-bond character than the C–O bond in SF. The oxygen of that bond is referred to here as the PHDF oxygen. SF corresponds to I in Me$_2$SO, and PHDF corresponds to I in methanol as more double-bond character is found in the former. Since R depends on NQCC, squared the relaxation rate would increase by a factor of $(7.311)^2/(5.644)^2 = 1.7$ in going from methanol to Me$_2$SO provided that the carboxylates are a good model for I. Including the effect of the asymmetry parameter decreases the factor by 0.2, but the magnitude is still large enough to constitute a potential source of error on the assumption that the ratio of relaxation rates is a measure of relative correlation times. Although the observed effects are dominated by correlation times, as has hitherto been assumed, we will now closely examine this assumption. The absolute magnitudes of the NQCCs of I in methanol and in Me$_2$SO are subject to considerable uncertainty, but from NQR in solids it seems to be fairly straightforward to discriminate between decrease and increase in the NQCC on small perturbations like hydrogen bonding.[26] The same probably holds also for the present case, and an increase may be predicted on going to Me$_2$SO as has been done above. If the NQCC changes appreciably, it is therefore expected to do so in a manner as to increse the line width, as does the increase in viscosity. As both these effects are counteracting, the effect by desolvation, what we see in Figure 3 is a curve where the effect of desolvation has been diminished by a possible change in the NQCC. The qualitative conclusion that something is happening to the effective size of the solvated complex already at low mole fractions of Me$_2$SO is therefore not in jeopardy. But it is possible to take the argument one step further. The assmption that the NQCCs of I and III do change with the solvent leads to unlikely consequences when the experimental data are interpreted and we find it most likely that the quadrupolar coupling constants do not change to any noticeable degree.

The basis for our conclusion is the experimental fact that R_I/R_{II} and R_{III}/R_{IV} are both essentially unity in Me$_2$SO. If there were a change in the NQCC of I and III, it would require a coincidental cancellation between the terms accounting for the correlation time

part and those accounting for the NQCC part to give relaxation rate ratios of unity. Or, even more unlikely, it could be explained by the possibility that the NQCCs of I and III do increase with Me$_2$SO concentration from values in methanol lower than those of II and IV to values in Me$_2$SO that exactly coincide with those of II and IV. This latter possibility requires that for total increases in the NQCCs of I and III by the factors x and y from methanol to Me$_2$SO the absolute magnitudes of the NQCCs of I and III in methanol are exactly $1/x$ and $1/y$ times those of II and IV.

It is not an attractive explanation of the data to suggest a number of coincidental cancellations—especially so since I and III are expected to exhibit large differences in behavior in terms of electron delocalization as a function of solvent composition. Such electron delocalization may be expected to affect the electric field gradient. Whereas I shows a pronounced shift of electron density from the phenolate oxygen into the ring, the corresponding effect with III must be small. The only conceivable source of a change in the NQCC of III is then the presence of very strong hydrogen bonds,[26] close to being symmetric. Because of the big difference in acidity between the hydrogen-bond donor methanol and the corresponding acid of III, benzoic acid, the hydrogen bond must be far from symmetric. Therefore a change in NQCC, if any, must be more pronounced in I than in III, and it is improbable that those effects would cancel out in the same way in two very different compounds.

Experimental evidence exists that supports a model of the methoxide ion in methanol as being hydrogen bonded to three solvent molecules.[21] It is also a reasonable model for most oxyanions provided that no steric hindrance reduces the accessibility to the charged oxygen atom. The results are compatible with this model and give the following physical picture. In methanol when the anions are fully solvated and the primary solvation shell is crowded, the methanol molecules hydrogen bond to the charged oxygen and their "tails" point straight out into the bulk solvent. The methyl groups of methanol are relatively inert and solvent molecules beyond these do not bind appreciably to the formed complex. As hydrogen-bonded molecules are removed by Me$_2$SO, the crowding decreases and the flexibility increases, the consequences being that on the average the tails are closer to the anion, effectively decreasing the size of the complex.

Formalisms are available for interpretation of chemical shift data of ions in mixed solvents in terms of preferential solvation, but as the basic assumptions for their use are not met in the present case, they are not valid here and no attempt has been made to use them.

In conclusion, then, we have shown that ^{17}O NMR is sensitive to differences in solvation of organic oxyanions and that qualitative conclusions can be drawn about the hydrogen-bonded molecules surrounding the anion. How sensitive it is and to what extent quantitative determinations can be made remain to be seen when more experimental data are available, for instance in other hydroxylic solvents or from sterically hindered systems. In the present investigation the anions of benzoic acid and 4-nitrophenol have been shown to be partly desolvated by Me$_2$SO in methanol already at relatively low mole fractions of Me$_2$SO, thereby confirming possibly controversial conclusions in earlier investigations.

(23) In linear free energy correlations, that can be found in most textbooks on physical-organic chemistry, the nitro group usually gives anomalous results when situated para to a developing, existing, or disappearing negative charge on an atom directly bonded to an aromatic ring. This is generally accepted as being due to strong delocalization of the negative charge toward the nitro group.

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