MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 356–358 (1998)

Nitro Group Effects on the ^1J(CC) Couplings in Nitroalkanes

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Received 13 October 1997; accepted 18 December 1997

ABSTRACT: One-bond ^{13}C–^{13}C coupling constants across a single bond are reported for a number of nitroalkanes including cases where two or three nitro groups are attached to the same carbon atom. The nitro group effect on the ^1J(CC) across the adjacent bond becomes significant when more than one nitro moiety is present at the same carbon, and it can amount to an increase in the coupling of 7 Hz, i.e. by about 20% with respect to a typical value of 35 Hz which is characteristic of unsubstituted alkanes. The effect is comparable to that exerted by chlorine substituents, but is smaller than those induced by hydroxy or alkoxy oxygen atoms and by fluorine. The results for nitroalkanes seem to suggest that a major factor in substituent-induced effects on ^1J(CC)s across a single bond is the electronegativity of the atoms which are attached directly to the bond, but some effects induced by methyl substituents suggest a contribution from steric hindrance. Semi-empirical calculations by the TNDO/2 method reproduced satisfactorily the general trends observed in substituent effects on ^1J(CC)s, including those exerted by nitro groups. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: nitroalkanes; spin–spin coupling; one-bond; carbon–carbon; substituent effects; calculations

INTRODUCTION

Whereas one-bond ^{13}C–^{13}C coupling constants across a triple bond are significantly affected by substituent effects and their values exhibit a fairly good linear relationship with the corresponding products of electronegativities of the atoms which are bound directly to the carbon–carbon triple bond concerned,[1] the situation is less clear for ^1J(CC)s across a double or single bond. As far as carbon–carbon single bonds are concerned, fluorine substituents have been shown to induce a remarkable increase in the coupling,[2] and the same but less pronounced trend has been observed for hydroxy and alkoxy substituents[3] and chlorine atoms.[4–6] This suggests at least some analogy with the much stronger effects observed in substituted acetylenes, but it is still unclear whether their origin lies essentially in the electronegativities of the atoms in the direct vicinity of the CC bond involved or, possibly, in the electron-withdrawing ability of the substituents where each is taken as a whole. The nitro group as a substituent of C—C bonds in alkanes seems to provide an interesting example, since the electronegativity of nitrogen is smaller than those of oxygen and fluorine, but the nitro moiety as a whole is known to be a strong acceptor of electron charge. We therefore elected to study the ^1J(CC)s in derivatives of nitroethane, including those bearing two or three nitro groups at the same carbon: $R^1R^2C(NO_2)$—$CR^3R^4R^5$.

So far, only a few sparse data have been published on three mononitroalkanes and these did not allow one to draw any definite conclusions about the influence of nitro substituents on carbon–carbon coupling across a single bond.[4]

RESULTS AND DISCUSSION

The nitroalkanes examined and the relevant values of the one-bond carbon–carbon couplings measured in the present work are shown in Table 1 together with some reference data for alkanes **1**–**3** and **7** and fluoroalkanes

Table 1. Experimental and calculated one-bond ^{13}C–^{13}C coupling in nitroalkanes

No.	Compound	Experimental ^1J(CC) (Hz)	TNDO/2-calculated Fermi contact contribution to ^1J(CC) (Hz)
1	$(CH_3)_4C$	33.7[a]	43.3
2	$(CH_3)_3CH$	35.0[a]	45.0
3	CH_3CH_3	34.6[a]	48.9
4	$CH_3CH_2NO_2$	35.6	48.4
5	$CH_3CH(NO_2)_2$	37.1	50.0
6	$CH_3C(NO_2)_3$	41.7	57.4
7	$CH_3CH_2CH_3$	34.6[a]	47.0
8	$(CH_3)_2CHNO_2$	36.3[a]	48.0
9	$(CH_3)_2C(NO_2)_2$	39.8	52.1
10	$(CH_3)_3CNO_2$	37.6[a]	48.4
11	$(CH_3)_2C(NO_2)Cl$	39.9	55.5
12	$(CH_3)_2C(NO_2)Br$	39.4	—[b]
13	$(CH_3)_2C(NO_2)I$	38.6	—[b]
14	CH_3CH_2F	38.2[a]	56.7
15	CH_3CF_3	60.5[a]	89.3

[a] Experimental couplings from Refs 1–5, and references cited therein.
[b] The scope of TNDO/2 does not extend over Br and I.

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CCC 0749-1581/98/050356–03 $17.50

14 and **15**, which should be helpful in assessing the significance of nitro group effects on ^1J(CC)s.

Unsubstituted alkanes show only little variation in their ^1J(CC) coupling constants (Table 1), less than ± 1 Hz with respect to a typical value of 34.5 Hz; thus the latter sets a convenient reference to substituent-induced effects on the coupling. It is interesting that ^1J(CC) in alkanes does not seem to respond significantly to branching of the hydrocarbon chain, i.e. it does not depend on whether the carbon atoms involved are primary, secondary, tertiary or quaternary. This insensitivity suggests that steric effects where only methyl groups are involved seem to play hardly any role in influencing the magnitude of ^1J(CC) across a single bond.

Nitroethane (**3**) shows only a weak increase in ^1J(CC), by about 1 Hz, with respect to ethane, but 2-nitropropane (**8**) and 2-nitro-2-methylpropane (**10**) reveal larger effects, about 2 and 3 Hz, respectively (Table 1). Hence a single nitro group seems to enhance slightly the coupling across the adjacent C—C bond, but the effect does not exceed 10% of the typical value for unsubstituted alkane systems. However, if one introduces two nitro groups at the same carbon, such as those in **5** and **9**, the effect becomes more pronounced, and in the case of three such nitro groups in **6** it attains a value of about 7 Hz, which corresponds to a 20% enhancement with respect to the average value of ^1J(CC) in alkanes (Table 1). In view of the foregoing, one can estimate the average effect on the relevant ^1J(CC) of a single nitro group as a 7% increase in the magnitude of the coupling. This is reasonably in accord with the experimental values obtained for mononitroalkanes and shows that the effects are fairly additive. Hence the nitro group, in view of the present results, does augment the ^1J(CC) coupling across the adjacent bond, and the rather weak effects observed in mononitroalkanes are not accidental.

We turn now to a comparison of the nitro group effects on ^1J(CC)s described above with those of some other substituents. The largest ones are induced by fluorine atoms[2] (see Table 1), and they do not seem to be exactly additive, but the average amounts to about a 20% enhancement per fluorine atom, about three times that observed for nitro substituents. The latter seem also to be slightly smaller than those exerted by OH and OCH_3 substituents,[3] e.g. ^1J(CC) in ethanol is 37.6 Hz and that in propylene-1,2-glycol is 41.3 Hz. Therefore, in view of the fact that the nitro group is a strong acceptor of electron charge while the increasing effects of substituents follow the sequence $NO_2 < OR < F$, which is consistent with that of Pauling's electronegativities[7] of the atoms which are bound directly to the C—C bond concerned, the latter factor seems to be dominant in the magnitude of substituent effects on ^1J(CC). This conclusion is corroborated by the absence of any significant contributions to ^1J(CC) in the case of carbonyl and SO_3H substituents.[1,4,6] The relevant values of the electronegativities are C 2.55, N 3.04, O 3.41 and F 3.98. The nitro group effects on ^1J(CC)s in alkane systems seem to be comparable to those exerted by chlorine substituents. For example, the coupling in 2,2-dinitropropane (**9**) matches almost exactly that in 2-chloro-2-nitropropane (**11**) (Table 1), and the coupling in 1,1,1-trinitroethane (**6**) (Table 1) is close to the literature value reported for 1,1,1-trichloroethane of 42.7 Hz.[1,2] Among the compounds studied in the present work there are three 2-halo-2-nitropropanes (**11**–**13**) (Table 1), and the small differences observed in their ^1J(CC)s are also consistent with the sequence of increasing electronegativity of the halogens, I (2.66) < Br (2.96) < Cl (3.16).[7] If we consider a series of 2-nitropropane derivatives having the general formula $(CH_3)_2C(X)NO_2$, where X = CH_3 (**10**), I (**13**), Br (**12**), NO_2 (**9**) and Cl (**11**), then a plot of their ^1J(CC)s (Table 1) against Pauling's electronegativities, E_P, of the atoms which are bound directly to the central carbon (C, I, Br, N and Cl, respectively) shows a reasonably good linear correlation (Fig. 1), expressed by the equation

$$J_{\text{experimental}} = 3.60E_P + 28.7 \qquad (1)$$

with a linear correlation coefficient $r = 0.97$ and a standard deviation of 0.3 Hz, in spite of the fact that the couplings concerned vary within a range of less than 3 Hz. Attention is drawn to the correct sequence of all of the ^1J(CC)s concerned with respect to that of the relevant E_Ps. Hence, in view of the foregoing, the nitro substituent effects on ^1J(CC)s across single C—C bonds seem to be those due to the nitrogen atom involved rather than those due to the presence of a strong electron acceptor as a substituent. The results of the present work provide an important argument in favor of the adjacent atom electronegativity as a major factor determining substituent effects on the CC coupling across a C(sp^3)—C(sp^3) bond.

It is interesting that methyl groups as substituents on C-1 in nitroethane (**4**) or 1,1-dinitroethane (**5**) seem to induce a weak increase in ^1J(CC), as can be observed in the following groups of compounds (Table 1):

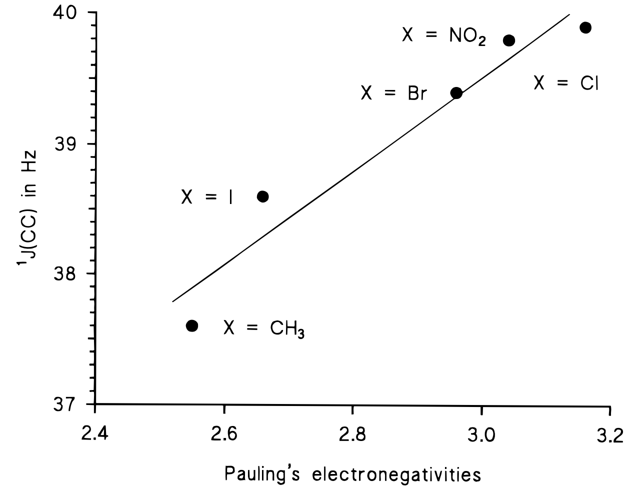

Figure 1. Experimental ^1J(CC)s in $(CH_3)_2C(X)NO_2$ compounds plotted against Pauling's electronegativities of those of the atoms in substituents X that are bound directly to the C—C bond concerned. The linear fit is described by Eqn (1).

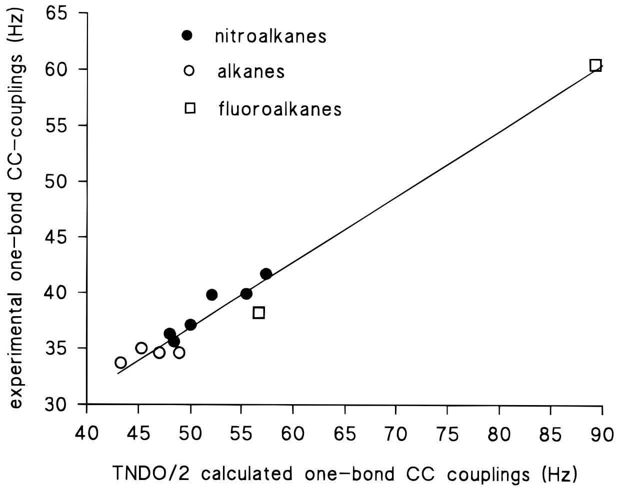

Figure 2. Plot of experimental values of $^1J(\mathrm{CC})$ coupling constants in alkanes, nitroalkanes and fluoroalkanes *vs.* TNDO/2-calculated Fermi contact contributions to the couplings. The least-squares fit is described by Eqn (2).

$\mathbf{4} < \mathbf{8} < \mathbf{10}$ and $\mathbf{5} < \mathbf{9}$. Since such effects fail to appear in the ^1J(CC)s of unsubstituted alkanes, it is likely that they stem from steric interactions between methyl and nitro substituents on the same carbon atom.

Finally, there is the question of how the observed trends in nitro group effects on one-bond CC coupling relate to quantum-mechanical calculations. We carried out the latter using semi-empirical methods, PM3 for geometry optimizations and TNDO/2 for the coupling (see Experimental), and we included the nitroalkanes considered, some unsubstituted alkanes as a reference group and some fluoroalkanes as a representation of the most pronounced effects of substituents. The results are reported in Table 1 in terms of the Fermi contact contributions to the coupling. The calculated values show a good linear correlation with the observed values (Fig. 2), as indicated by the regression equation

$$J_{\text{experimental}} = 0.590 J_{\text{calcd}} + 7.4 \qquad (2)$$

with a linear correlation coefficient $r = 0.99$ and a standard deviation of 1.2 Hz or about 2% of the observed range of the coupling. The calculations reproduce correctly the range of nitro group effects on ^1J(CC)s in alkane systems with respect to that of fluorine-induced effects, but they also reflect some finer details within the nitroalkane ^1J(CC)s considered, including the effect of the increasing number of nitro substituents at the same carbon atom.

EXPERIMENTAL

Some of the compounds studied were commercially available CP-grade products and the other were prepared by published procedures: **5**,[8] **6**,[9] **9**,[10] **11**,[11] **12**[11] and **13**.[11] The ^{13}C–^{13}C spin–spin coupling constants were measured at the natural abundance of the isotope using 50% (v/v) solutions in $CDCl_3$; the latter provided a source of deuterium lock. The proton-decoupled one-dimensional INADEQUATE spectra were measured at 125.76 MHz (^{13}C) or 500 MHz (^{1}H) using a Bruker AM-500 system and its standard software procedure INADEQ..AUR (32-phase Freeman cycle with automatic data storage). Typical conditions included an acquisition time of 2.4–6.2 s, a digital resolution of 0.16–0.25 Hz per point and 215 cycles in 12 h. Quantum-mechanical calculations of the spin–spin couplings concerned were carried out on a Pentium-S (200 MHz)-based system. The molecular geometries were optimized using the semi-empirical PM3 method, which is known to yield reliable results for polar molecules. The couplings were calculated by the TNDO/2 method devised at Hypercube (Waterloo, ON, Canada); it is a modification of the INDO method, by introducing parametrizations which are not unique for a given element, but are subdivided into a number of 'types,' depending on the type of bonding involved. The method is implemented and described in their HyperNMR software suite which we employed in our computations of the spin–spin couplings, in conjunction with the HyperChem 4.0 package for geometry calculations.

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