^{13}C NMR Chemical Shifts in Donor—Acceptor Systems. A Model for the Alternating Substituent Effect

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^{13}C chemical shifts in three donor-acceptor substituted ethylenes respond characteristically to changes of the donor substituents. An increased electron donating capacity causes downfield shifts for atoms removed from the donor atoms by an odd number of bonds and upfield shifts for atoms removed by an even number of bonds. The shifts are qualitatively predicted by a simple perturbation MO model which also applies to other molecules with donor atoms adjacent to a π-system.

A great deal of attention has been focused on the effects of substitution on ^{13}C chemical shifts. Recently, several papers have reported on systems, saturated as well as unsaturated, where this effect is alternating along a carbon chain.[1-5] These examples of alternating substituent effects may be rationalized on the basis of charge alternation predicted by CNDO[6] as well as *ab initio* calculations.[7] In the present communication we present the result of a ^{13}C NMR study of a series of donor—acceptor systems ($1-3$, $a-c$), which show pronounced alternating chemical shift changes along the carbon chain C-1 — C-3(C-3′) upon change of the C-1 sulfur substituent (see Table 1). In donor—acceptor systems electron density is transferred from a donor group (the sulfur substituent) to an acceptor group (the remaining molecule). These compounds can therefore not immediately be subjected to treatments that neglect charge transfer effects as in Ref. 8. As an alternative treatment we suggest that induced charge variations in series of related systems of the donor—acceptor type may be predicted approximately by applying second-order perturbation theory to the charge transfer process.
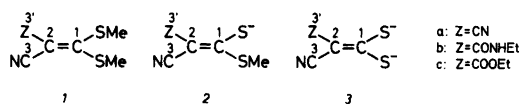
EXPERIMENTAL

Compounds 1 ($a-c$) and *3* ($a-c$) were obtained by literature methods.[9] Compounds *2* ($a-c$) were prepared as sodium salts by treatment of *3* ($a-c$) with equimolar amounts of methyl iodide in aqueous methanol. They were isolated as a mixture with sodium iodide by evaporation of the reaction mixture, dissolution in acetone, filtration and precipitation with methylene chloride. No organic contaminants were detected on the basis of the ^{1}H NMR spectra of these products. Noise decoupled ^{13}C NMR spectra were determined with a Bruker WH 90 NMR instrument. All samples were examined at *ca.* 35 °C in DMSO-d_6 solution (~0.5 M) and shieldings measured relative to TMS. Unambiguous signal assignments were made by comparison with spectra of compounds *1c—3c* specicifically ^{13}C labeled at C-1, prepared from ethyl cyanoacetate and ^{13}CS$_2$.[9]

RESULTS AND DISCUSSION

The ^{13}C NMR results (see Table 1) in each of the three series ($a-c$) clearly demonstrate the following: C-1 becomes progressively more deshielded in going from neutral to dianionic species. A downfield shift of ~45 ppm at C-1 upon increasing electron-donating power of the substituent is remarkable. This places the actual chemical shift of C-1 in the dianion at the very low-field end of the chemical shift scale (~220 ppm) in spite of the gross negative

Table 1. ^{13}C chemical shifts in ppm relative to TMS.

	1a	2a	3a	1b	2b	3b	1c	2c	3c
C-1	185.7	202.5	224.6	166.8	190.1	214.3	181.2	203.7	225.6
C-2	74.4	64.0	67.5	106.3	95.1	96.6	98.2	89.0	90.2
C-3	113.1	119.6^a	123.5	116.1	121.0	127.4	115.9	122.2	125.8
C-3'	113.1	118.3^a	123.5	160.5	165.6	167.9	161.5	164.7	166.7

^{a} Shift assignments may be interchanged.

charge of this species. Shifts towards lower field are also observed for the carbon atoms 3 and 3'. C-2, separated by two bonds from the donor centers, becomes more shielded in going from neutral to charged species, but is slightly less shielded in the dianion than in the monoanion. If these features of ^{13}C shifts are interpreted in terms of charge density variations,* the charge redistribution induced by *increasing* the electron donating power of the sulfur substituent (going from *1* to *3*) results in *decreased* charge density on the carbon atoms one and three bonds removed from the substituent.

Considering the theoretical predictions[6,7] that a small amount of charge transfer implicates an additional charge separation, the perturbation model can be used on the charge transfer process in donor—acceptor systems. In the perturbation approach charge transfer is equivalent to interactions between occupied and unoccupied substructure orbitals and orbital interactions are inversely proportional to the energy difference between the interacting orbitals. While there is usually a large energy gap between occupied and unoccupied substructure orbitals in organic compounds, donor acceptor systems are characterized by a relatively small energy difference between the donor HOMO and acceptor LUMO. The perturbation treatment suggests that the interaction of these two orbitals which is most heavily felt in the compound HOMO[11] is the major source of transfer and, thereby, of charge separation. As a consequence the induced charge variations in these systems may be predicted approximately by evaluating the

changes in the compound HOMO which results from changing the (donor) substituent (going from *1* to *3*) keeping the remaining substructure constant. The compound HOMO can be represented as the donor (the sulfur substituent) HOMO combined out-of-phase with the acceptor (the remaining molecule) HOMO and incorporating a smaller in-phase contribution from acceptor LUMO. This is shown for the systems *1a—3a* in Fig. 1; phase and relative amplitudes at each atom are represented by the vectors. The successive replacement of two CH_3S- with S^- donors through the series *1—3* increases the donor-HOMO energy by concentrating electron density on sulfur. The predicted result of this change is an increased incorporation of acceptor LUMO leading to increased charge transfer. At the same time the compound HOMO is depleted at C-1 and C-3 where acceptors HOMO and LUMO are out-of-phase (vectors in opposite direction) and concentrated on C-2 and N where these orbitals are in phase. These changes are in accord with the observed ^{13}C NMR results assum-

* An alternative interpretation would involve a predominating contribution from *changes* in the mean electronic excitation energy.[10] This alternative seems unlikely as the absorption spectra are largely unchanged through each of the series *1—3*, e.g. $\lambda_{max} = 334$, 341, and 342 nm for *1c*, *2c*, and *3c*, respectively and CNDO calculations[12] show only a small shift in the lowest $n \rightarrow \pi^*$ transition while they predict the development of positive charge at C-1.
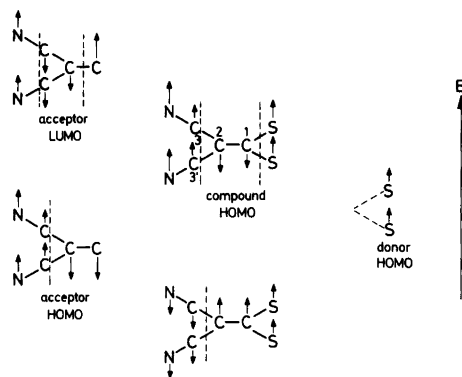

Fig. 1. Combination of donor and acceptor substructure orbitals to give compound HOMO. Phase and relative amplitude at each atom are represented by the vectors.

ing that chemical shift changes are influenced primarily by charge density variations. The model does not predict the slight but consistent upfield shift at C-2 in the monoanion relative to the dianion but neither does the CNDO calculation of total charge.[12] However, it should be noted that both models operate on the isolated molecule and do not include medium effects.

The range of applicability of this approach has been tested against data from the literature. The model presented here predicts the variation in ^{13}C NMR substituent shifts for donor substituted ethylenes,[5] butadienes,[1] and arenes.[13] The observed attenuation in the two latter systems does not emerge from this simple picture. However, already the introduction into the interaction scheme of the subjacent unoccupied orbital of the skeleton substructure will bring forth such an effect.

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