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A CNDO/2 EVALUATION OF SUBSTITUENT EFFECTS ON THE CHARGE DISTRIBUTION OF CONJUGATED IONS

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Abstract—The CNDO/2-SCFMO method is used to evaluate the effect of the Me group on the charge distribution and relative stabilities of the conjugated ions with an odd number of atoms in the chain. The Me group is electron withdrawing when substituted on a conjugated carbanion, while it is electron donating relative to hydrogen when substituted on a conjugated carbonium ion. Comparison of the charge densities of the terminal methylene atoms of the *trans*-1,3-pentadienyl anion with the terminal methylene atoms of either *cis*- or *trans*-1-methyl-1, 3-penta-dienyl anions shows that the Me group has no effect on these densities. *cis*-1-Methylallyl anion is calculated to be more stable than the *trans*-isomer by about 1·0 kcal/mole, while the *trans*-1-methylallyl cation is predicted to be 4·2 kcal/mole more stable than the *cis*-isomer. The predicted relative stabilities agree with experimental observations. Of the two possible enolate anions derived from 2-butanone, the most highly substituted anion was more stable by 11·0 kcal/mole.

A GROWING controversy[1–4] over the electronic nature of the Me group as a substituent has arisen. In view of a wide range of experimental and theoretical observations the Me group is best considered as polarizable.[5–7] Our calculations on the 1-methylallyl anions and cations definitely support this conclusion.

Recently, the NMR spectra[8–16] of a large number of conjugated anions have been published and attempts have been made to correlate the observed proton chemical shifts and coupling constants with π-electron densities and bond orders calculated using HMO theory. Kloosterziel[14] has interpreted the chemical shifts of *cis*- and *trans*-1-methylpentadienyl anions on the assumption that the Me group is electron releasing. Bank[17,18] has proposed an electron donating Me group as the source of the relative stabilities of *cis*- and *trans*-1-methylallyl anions. Alkyl substitution[19] is reputed to destabilize negative charge on the α-C atom of enolate anions in the belief that alkyl groups are electron donating.

However, the Me[6] group has been shown to be electron withdrawing when bonded to aromatic sp^2 carbon which is negatively charged. Yet, Streitwieser[20,21] believes that the CNDO/2 method overemphasizes electron–electron repulsion so that the electron withdrawing effect of the Me group of 4-methylbenzyl anion is exaggerated.

In view of our success[22] in correlating proton chemical shifts with the electron densities of hydrogens, we decided to evaluate the effect of the Me group on the charge distribution and relative stabilities of some conjugated ions using the CNDO/2[23,24] method in order to gain a theoretical insight into the problem. Standard geometries were used throughout the calculations. All trigonal C—C distances are 1·40 Å, C—O distances are 1·29 Å, and C—S distances are 1·68 Å except where noted.

RESULTS AND DISCUSSION

(a) *Charge distribution*

When the terminal methylene group of the allyl, pentadienyl, and heptatrienyl anions is replaced by oxygen or sulfur the total charge and π-charge density increase on the heteroatom. The charge on sulfur is larger than on oxygen when thioenolate and 1-thiapentadienyl anion are compared with enolate and 1-oxapentadienyl, respectively.

Examination of Table 1 shows that of the total π-electron density withdrawn by oxygen approximately 50% is withdrawn from the C atom adjacent oxygen. However, 90% of the π-electron density withdrawn by the S atom of the thioenolate anion is withdrawn from the terminal C atom. In the 1-thiapentadienylate case, more π-electron density is withdrawn from the terminal carbon than from the carbon adjacent sulfur. Sulfur withdraws most of the π-electron density from the C atoms which are negatively charged in the formal resonance structures of 1-thiapentadienylate.

TABLE 1. π-CHARGE WITHDRAWN FROM CARBON ATOMS[a]

Compound	Atom	C_1	C_2	C_3	C_4	C_5	C_6
Allyl	O	0·0508	0·0654	—	—	—	—
	S	0·0314	0·2867	—	—	—	—
Pentadienyl	O	0·0774	0·0310	0·0078	0·0376	—	—
	S	0·0924	0·1797	−0·0130	0·1437	—	—
Heptatrienyl	O	0·0920	0·0079	0·0211	0·0260	−0·0027	0·0291

[a] d-orbitals are not included.

The total charge on the carbon adjacent to the O atom is twice as positive as the carbon adjacent to the S atom; therefore it is not surprising that the most negative C atom of the oxygen anions is the number two carbon from oxygen. However, in the sulfur anion the terminal carbon is the most negatively charged of all C atoms.

The S atom appears to be more electron withdrawing than oxygen. The reason sulfur has a higher negative charge than oxygen is the larger size of the sulfur anion than oxygen. The negative charge on sulfur is more diffuse than on oxygen. Also, the overlap between the $3p_z$ orbital of sulfur and the $2p_z$ orbital of carbon is smaller than the $2p_z$–$2p_z$ overlap of oxygen and carbon. For example, the π-bond order of the C—S bond of the thioenolate is a little more than half the bond order of the C—O bond order of the enolate anion. The poorer overlap is probably due to the fact that the C—S bond is almost 0·4 Å longer than the C—O bond as well as the fact that the two pπ orbitals of the C—S bond are of different principal quantum numbers.

Comparing the bond orders of pentadienylate, 1-oxapentadienylate, and the 1-thiapentadienylate anions shows that while the last anion has little double bond character for the C—S bond, the C—O bond and the terminal C—C bonds have more double bond character than the two center C—C bonds.

Recently, the NMR spectra[14–16] of the pentadienylate, 1-oxapentadienylate, and the 1-thiapentadienylate anions have been recorded. The proton resonances of the terminal methylene of the *cis*-1-thiapentadienylate are shifted downfield from those of the terminal methylene of the *cis*-1-oxapentadienylate which shows little difference in the shifts from *trans*-1-oxapentadienylate anion. The resonances of the terminal hydrogens of *trans*-1-oxapentadienylate are about 1·00 ppm downfield from those of the terminal methylene of the *trans*-pentadienylate anion. Examination of Table 2

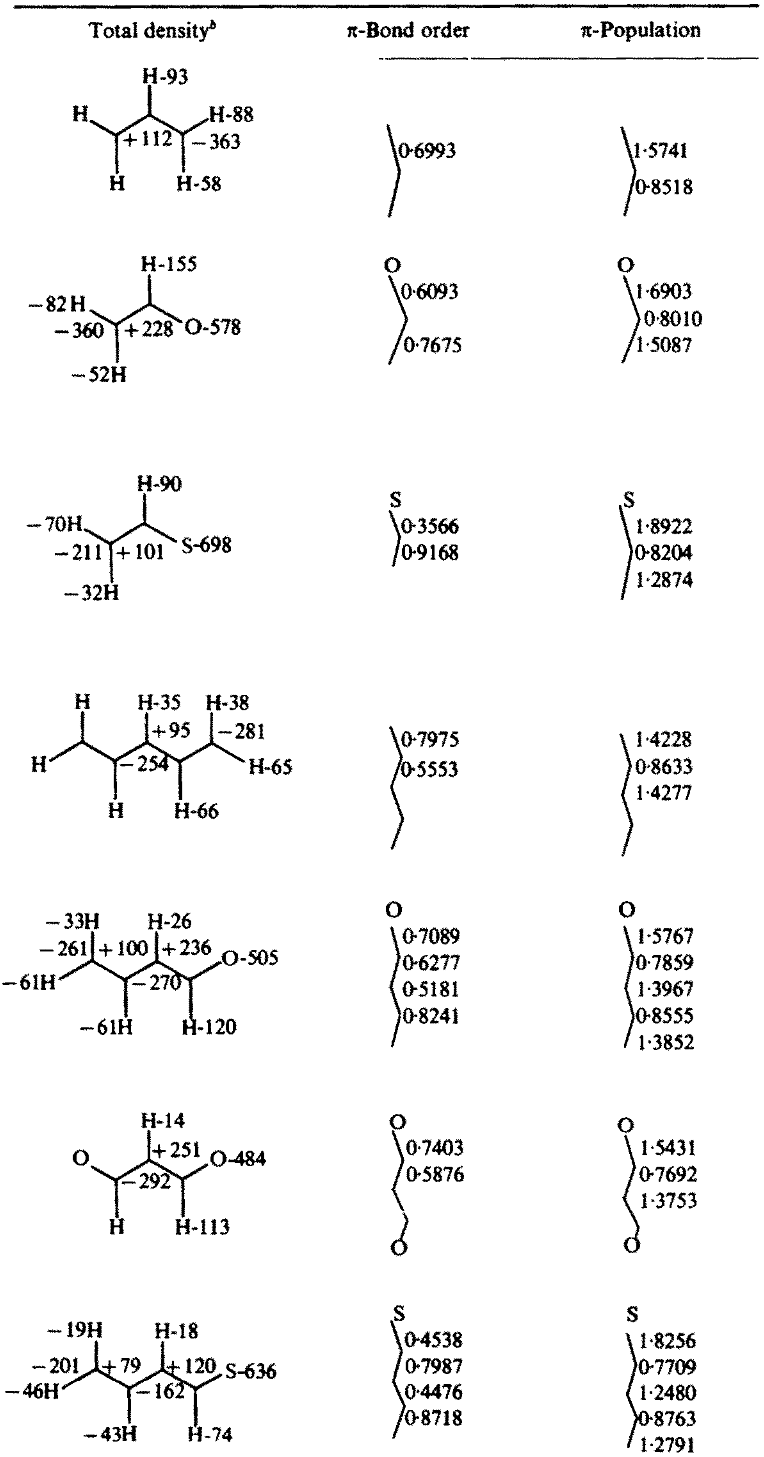
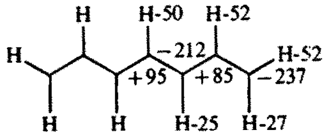
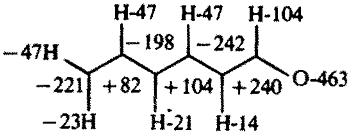


FIG 1. Total density and π-density of anions[a]

FIG 1 (*continued*)

Total density[b]	π-Bond order	π-Population
	0·8352 0·5050 0·6552	1·3448 0·8760 1·3505 0·8575
	O 0·7510 0·5758 0·6080 0·6925 0·4850 0·8500	O 1·5182 0·7840 1·3426 0·8364 1·3245 0·8787 1·3157

[a] d-orbitals are not included

[b] Total density are 10^{-3} electrons

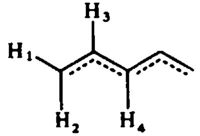
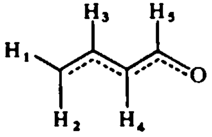
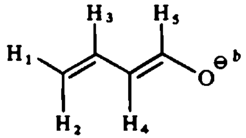
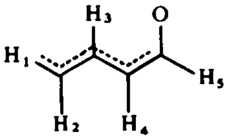
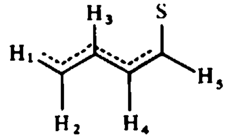
shows that only a qualitative relationship exists between the electron densities on the hydrogens and the observed chemical shifts and the closer the hydrogen is to a heteroatom the worse this relationship gets. The number one hydrogen is always upfield from the number two hydrogen and the electron density on hydrogen one is always larger than on hydrogen two. However, the number three hydrogen is always downfield from the number two hydrogen while the electron density of the number three hydrogen is always larger than hydrogen two. For hydrogens one, two, and three the downfield shift correlates roughly with a decrease in electron density when the various ions are compared. However, when hydrogens four and five are compared no relationship exists. Evidently, the anisotropy effect of the heteroatom swamps out the charge distribution effect. In addition, these calculations neglect the effect of the counter ion which is most likely associated with the heteroatom.

The substituent effect of the Me group is a function of position and anion structure. The specific systems considered are listed in Table 2.

To test the effect of Me geometry on the charge densities on C and H atoms of selected anions, two sets of calculations were made: one with a C—H bond of the Me group oriented *in* the nuclear plane of the molecule and one with a C—H bond perpendicular to the molecular plane. The effect of Me conformation on the electronic substituent effect of the Me group is shown in Table 3. The results show there is little or no effect of Me conformation on the ability of a Me group to donate or withdraw electrons to or from the parent system. In fact, there is virtually no change in the total electron densities on all atoms of the anion except for the hydrogens of the substituent Me group. In the latter case, the total net charge on the Me group of each orientation is essentially the same.

The choice of C—C bond lengths for the C(sp^2)—C(sp^2) bonds had only a small effect on the substituent effect of the methyl group (Table 3).

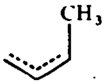
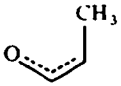
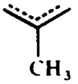
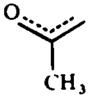
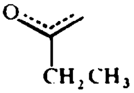
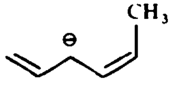
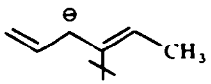
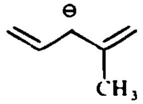
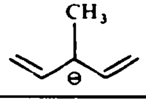
TABLE 2. CHEMICAL SHIFTS[a] AND CHARGE DENSITIES OF THE HYDROGEN ATOMS OF THE PENTADIENYLATE ANIONS

	σH_1	σH_2	σH_3	σH_4	σH_5	q_1	q_2	q_3	q_4	q_5
	2·58	3·01	6·13	4·35	6·13	−0·065	−0·038	−0·066	−0·035	−0·066
	3·78	4·11	6·35	4·82	7·79	−0·061	−0·033	−0·065	−0·027	−0·139
	—	—	—	—	—	−0·060	−0·029	−0·054	−0·029	−0·137
	3·86	4·22	6·82	4·30	7·32	−0·060	−0·036	−0·039	−0·054	−0·133
	4·55	4·72	7·20	5·81	7·05	−0·045	−0·026	−0·006	−0·055	−0·083

[a] Chemical shifts are relative to TMS σ = 0·00 ppm

[b] Double bonds C═C = 1·34 Å, single bonds C—C = 1·46 Å and C—O = 1·29 Å

TABLE 3. ELECTRONIC EFFECT OF THE METHYL GROUP ON ANIONS

Compound	Electrons withdrawn by methyl	Electrons withdrawn (donated) from (to) π-System
	0·102 0·102^{a} 0·108^{b}	0·052 0·049^{a} 0·051^{b}
	0·100 0·098^{a} 0·100^{b}	0·055 0·055^{a} 0·055^{b}
	0·094 0·093^{a} 0·093^{b}	0·042 0·043^{a} 0·043^{b}
	0·091 0·093^{a} 0·093^{b}	0·045 0·046^{a} 0·045^{b}
	0·030 0·030^{b}	(0·008) (0·008)^{b}
	0·009 0·009^{a} 0·009^{b}	(0·013) (0·013)^{a} (0·013)^{b}
	0·018^{b}	(0·017)^{b}
	0·076 0·075^{a} 0·074^{b}	0·033 0·031^{a} 0·033^{b}
	0·076 0·077^{a} 0·076^{b}	0·036 0·036^{a} 0·036^{b}
	0·069	0·027
	0·067	0·030
	0·028	(0·010)
	0·089^{b}	0·044^{b}

[a] One of the C—H bonds is eclipsed by the C—C bond.

[b] One of the C—H bonds is perpendicular to the nuclear plane.

[c] Where double bonds are indicated the C—C length is 1·34 Å otherwise 1·46 Å.

Therefore, with respect to the discussion on the electronic substituent effect of the Me group, the precise choice of C—C bond length and Me conformation appear to be not critical to the conclusions drawn. The orientation of the Me group assumed in the following discussion is the one with a C—H bond of the Me group *in* the nuclear plane.

Allyl anion. Compared with hydrogen, the Me group at the 1-position is an electron withdrawing substituent. The Me moiety of *cis*-1-methylallyl anion withdraws, relative to the corresponding hydrogen of the allyl anion, a total of 0·102 electrons of which 0·051 electrons came from the allyl π-system. The effect noted for the Me group in *trans*-1-methylallyl anion is virtually the same. Here the Me group withdraws 0·100 electrons, with 0·055 electrons coming from the π-system. In contrast, the *net* effect of a Me group in the 2-position is to withdraw only 0·030 electrons. There is a slight donation of charge (0·008 electrons) to the π-system which is more than offset by the withdrawal of 0·038 electrons from the σ-system.

The charge distribution on the C atoms is smoothed out by a 1-Me substituent (*cis* or *trans*); the negative charges at C_1 and C_3 are reduced (the effect being greatest at C_1) with a slight reduction of positive charge at C_2. A 2-Me group increases the positive charge density at C_2 but has virtually no effect at the terminal C atoms.

A *cis* or *trans* 1-Me group decreases the C_1—C_2 π-bond order and increases the C_2—C_3 bond order. A 2-Me moiety reduces the bond orders of both C_1—C_2 and C_2—C_3.

Pentadienyl anion. Relative to hydrogen a *cis* or *trans* Me group in the 1-position is electron withdrawing. The substituent Me (*cis* or *trans*) moiety withdraws a net 0·076 electrons (somewhat less than the effect noted for the Me group in 1-methylallyl anion) with nearly half this value (0·033 for *cis* and 0·036 electrons for *trans*) coming from the pentadienyl π-system. Calculations assuming C_1—C_2 and C_4—C_5 bond lengths of 1·34 Å and C_2—C_3 and C_3—C_4 bond lengths of 1·46 Å yielded similar results; the 1-Me group withdraws 0·067 to 0·069 electrons with 0·027 to 0·030 electrons coming from the π-system. With the latter geometry a 2-Me substituent gave a significantly diminished effect, withdrawing a net 0·028 electrons. The 2-Me group donated 0·010 electrons to the π-system but this was more than compensated for by the withdrawing effect of the sigma system. The 3-Me moiety withdraws a total of 0·089 electrons with 0·044 electrons coming from the π-system, behavior which is similar to that of the 1-Me group.

A 1-Me group (*cis* or *trans*) reduces the magnitude of the charge density at all C atoms thereby smoothing out the charges. A 3-Me substituent yields a similar effect. However, a 2-Me group affects significantly only the C_2 charge density; an increase in positive charge density at C_2 is observed upon Me substitution.

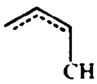
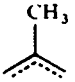
The effect of a 1-Me group (*cis* or *trans*) is to increase the C_2—C_3 and C_4—C_5 bond orders and decrease the C_1—C_2 and C_3—C_4 bond orders. A 2-Me group increases the C_4—C_5 bond order and reduces the other three. Finally, a 3-Me substituent increases the C_1—C_2 and C_4—C_5 bond orders.

Enolate anion. The effect of a 1-Me group (methyl bonded to the carbonyl carbon) on the carbon and oxygen charge densities is virtually negligible. The 1-Me substituent withdraws a net 0·009 electrons. There is some donation to the π-system (0·013 electrons) which is more than compensated by the electron withdrawal (0·022 electrons) via the sigma system. In contrast, the 2-Me group enjoys an electron-withdrawing power (0·091 electrons for *trans* and 0·094 electrons for *cis*) comparable with the similarly positioned Me groups of 1-methylallyl and 1- or 3-Me pentadienyl anions.

A *trans* 1-Me group reduces the magnitude of the charge density on C_1 and the hydrogens bonded to C_1 and C_2. The charge density on C_2 and oxygen are nearly unchanged. A *cis* Me group reduces the magnitude of the charge density at C_1, oxygen, and the hydrogens bonded to C_1 and C_2. The charge density on C_2 is unchanged.

Both the C_1—C_2 and C_1—O bond orders of the enolate anion are reduced slightly by a 1-Me substituent. However, the 2-Me group increases the C_1—O π-bond order and decreases the C_1—C_2 π-bond order of the enolate anion.

TABLE 4. ELECTRONIC EFFECT OF THE METHYL GROUP ON THE ALLYL CATION

Compound	Electrons donated by methyl	Electrons donated to π-system
	0·115	0·121
	0·111	0·109
	0·030[a]	0·018[a]

[a] One of the C—H bonds of methyl is perpendicular to the nuclear plane

The effect of a Me group substituted on the allyl cation is summarized in Table 4 for contrast. A Me group in the 1-position (*cis* or *trans*) is electron donating relative to hydrogen with virtually the total effect attributable to electron donation via the π-system. The C atom to which the Me group is attached has a higher *positive* charge density than the corresponding atom in the allyl cation while the C atom β to the Me group has a higher *negative* charge density than the 2-C atom in the unsubstituted cation. The magnitude of electron donation by the Me group is quite similar to the magnitude of electron withdrawal of a Me group in 1-methylallyl anion (*cis* or *trans*) noted previously (Table 3). However, the mechanisms of charge transfer appear to be different.

A 2-Me substituent is also an electron donating substituent but to a much smaller extent than observed for a 1-Me group. Slightly more than half (0·018 out of 0·030 electrons) is donated to the π-system. The charge on the 2-carbon is positive in 2-methylallyl cation but negative in 1-methylallyl and allyl cations. The positive charge density at the 1- and 3-C atoms is reduced by the 2-Me substituent. The H atoms have a lower positive charge density in the Me substituted cations than in the allyl cation.

A 1-Me group (*cis* or *trans*) reduces the C_1—C_2 π-bond order. A 2-Me moiety decreases both the C_1—C_2 and C_2—C_3 π-bond orders.

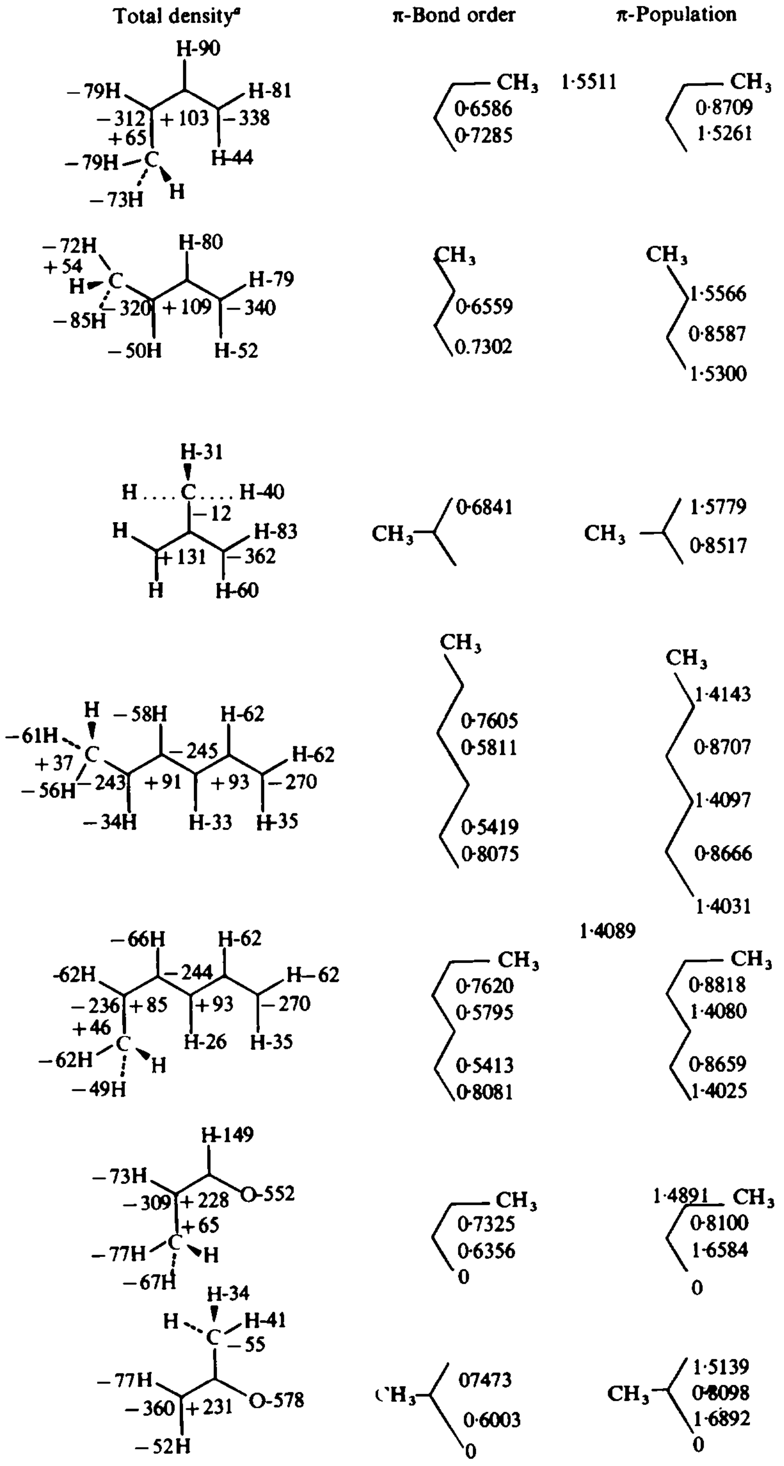
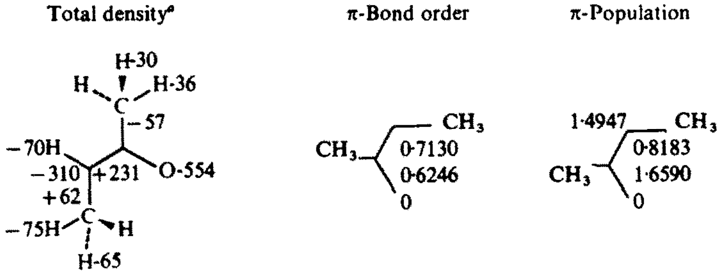


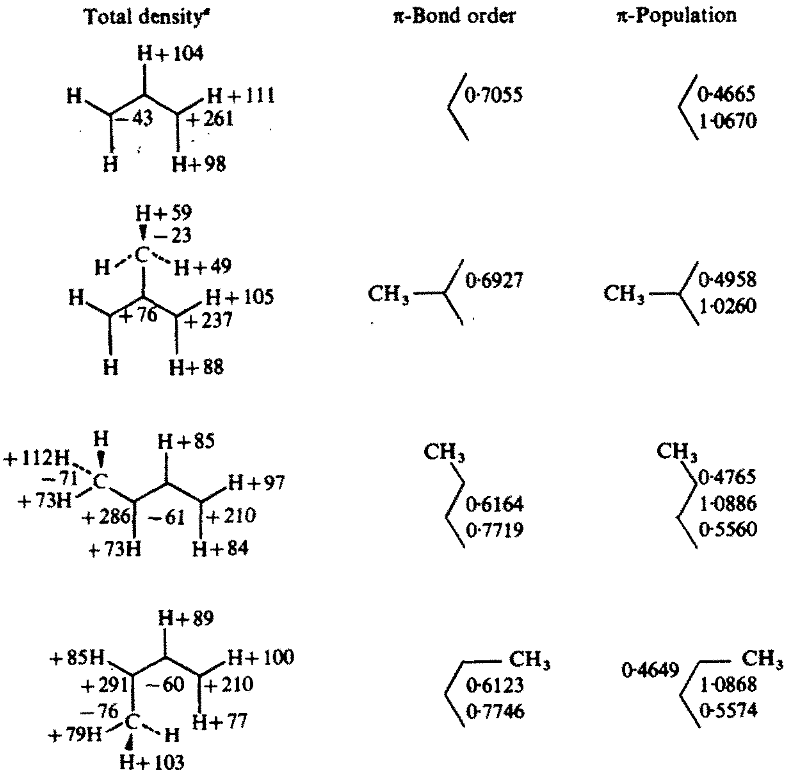
FIG 2. Total density and π-density of methyl substituted anions

Fig 2 (*continued*)



[a] Total densities are 10^{-3} electrons

The results presented in this paper suggest that a Me group may withdraw as well as donate electrons. When a Me group is attached to a C atom bearing substantial negative charge density the Me group becomes an electron acceptor while a Me group attached to a highly cationic carbon atom donates negative charge. This view,



[a] Total densities are 10^{-3} electrons

FIG 3. Total density and π-density of cations in fact, has been suggested previously in various forms.[3, 5, 7, 25, 26] Our data imply in addition that the electronic substituent effect of a Me group is dependent upon its location within a molecule.

The NMR spectra of both pentadienyl anion and *trans*-1-methyl pentadienyl anion have been reported in the literature.[9, 11, 14] The protons attached to the C_5 C atom of *trans*-1-methyl pentadienyl anion were shifted upfield by about 0·3–0·4 ppm relative to the corresponding protons of pentadienyl anion. The observed upfield shift was ascribed to a charge-repelling effect of the Me group.[14] It was suggested that the *trans*-Me group repels more charge than the *cis*-Me group.[14] The CNDO/2 calculated electron densities on the C_5 C atom of *trans*-(or-*cis*)-1-methylpentadienyl anion and the attached H atoms are very slightly more positive than the densities obtained for the corresponding atoms of pentadienyl anion. These calculated densities do not support the hypothesis that the upfield shift observed is a result of a charge-repelling effect. The recently observed[22] correlation of hydrogen electron densities with proton chemical shifts for some aromatic ions suggests that the calculated CNDO/2 densities are reasonable. It is not possible, however, to calculate the order of the proton shifts in the unsaturated ions considered here since the differences in the electron densities on the protons within a given ion are small. In this situation, one expects long-range shielding effects to control the order of the shifts. It is worth noting that the chemical shifts of the protons attached to sp^2 carbon in some Me substituted allyl cations[27, 28] are found significantly downfield from the proton resonances observed for the allyl anion.[8] The resonances of the unsubstituted allyl cation would be expected to be even farther downfield. These observations are in qualitative agreement with predictions based on the CNDO/2 calculated charge densities of the H atoms of the allyl cation and anion. The explanation for the small upfield shift on Me substitution is unclear but differences in ion association and/or variation in the binding position of the cation may be, in part, responsible. In view of the reversal of the order of acidities of some simple alcohols in the gas phase as compared with solution[25] it seems risky to attribute the small upfield shift observed to the substituent effect of an isolated Me group.

The efficiency of a Me group in either electron donation or electron withdrawal appears to depend on the magnitude of the charge on the carbon to which the Me moiety is attached. In the pentadienyl and allyl ions the odd numbered C atoms have a charge density which is much larger (and opposite in sign) than the even numbered C atoms. The electronic substituent effect of Me groups attached to odd C atoms is significantly greater than Me groups attached to even C atoms (Tables 3 and 4).

(b) *Energy*

Examination of Table 5 shows that *cis*-1-oxapentadienylate is more stable than the *trans* isomer. This relationship holds for the 1-thiapentadienylate anions, also. Furthermore, *cis,trans*-1,5-dioxapentadienylate anion is calculated to be more stable than either the *trans,trans* or *cis,cis* anion. The relative instability of the *cis,cis* anion is due to the repulsion between the two O atoms. The stability of the *cis,trans*-1,5-dioxapentadienylate anion is probably due to an electrostatic attraction between the negatively charged heteroatoms and the positively charged C atom which is three atoms away from the heteroatom. Experimental observations[16, 29] tend to confirm the relative stabilities in a qualitative manner.

Table 5 also reveals that 2-alkyl enolate and allyl anions are about 7·0 kcal/mole less stable than the *cis*-1-alkyl enolate and allyl anions which are about 1·0 kcal/mole more stable than the *trans*-isomers. The latter observation is true for 1-methylpentadienylate anions. Conversely, the *trans*-1-methylallyl cation is calculated to be about 4·2 kcal/mole more stable than the *cis* isomer. Again these calculated stabilities agree with experimental observations.[17,27]

Table 5. Relative stabilities of the ions[a]

Compound	Total energy (au)	Relative energy (kc/m)
cis-3-Methylenolate anion	43·364218	0·0000
trans-3-Methylenolate anion	43·363142	0·6774
2-Methylenolate anion	43·353075	6·9899
trans-2,3-Dimethylenolate anion	52·064828	0·0000
2-Ethylenolate anion	52·047162	11·0879
cis-1-Oxapentadienylate anion	50·352470	0·0000
trans-1-Oxapentadienylate anion	50·351034	0·9036
cis,trans-1,5-Dioxapentadienylate anion	60·169281	0·0000
trans,trans-1,5-Dioxapentadienylate anion	60·168471	0·5083
cis,cis-1,5-Dioxapentadienylate anion	60·163736	3·4827
cis-1-Thiapentadienylate anion	42·911685	0·0000
trans-1-Thiapentadienylate anion	42·907246	2·7861
cis-1-Methylallyl anion	33·537047	0·0000
trans-1-Methylallyl anion	33·536067	0·6146
2-Methylallyl anion	33·525756	7·0840
trans-1-Methylallyl cation	33·216445	0·0000
cis-1-Methylallyl cation	33·209715	4·2231
2-Methylallyl cation	33·174297	26·4495
cis-1-Methylpentadienylate anion	49·240218	0·0000
trans-1-Methylpentadienylate anion	49·239502	0·4518

[a] Relative energies which are reported as 0·0000 correspond to the most stable isomers

The explanation of the relative stabilities of the 1-alkylallyl anions and cations has in the past been based on the assumption that the Me group is electron releasing and is therefore positively charged. These calculations show that while the Me group is electron donating in the allyl cation, a fact which lends credence to an electrostatic explanation for the relative stabilities of the cations, the Me group is electron withdrawing and is therefore negatively charged in the anions. It does not seem probable that the simple electrostatic argument proposed by Bank accounts for the fact that the *cis*-1-methylallyl anion is more stable than the *trans* isomer. Without a more detailed analysis of the energies of the non-bonded interactions between the Me group and the negatively charged terminal methylene, it is not possible to account for the calculated stabilities of these anions on a simple basis.

An interesting question which arises in the chemistry of enolate anions is the effect of alkyl substitution at the α-C atom. In the past it has been argued that alkyl substitution on a negatively charged atom destabilizes the molecule on the assumption that the alkyl group is electron releasing.[19] However, the negative charge associated with an enolate anion tends to reside more on oxygen leading to the contention that the carbon–carbon bond has considerable double bond character which is stabilized by alkyl substitution. Indeed, the CNDO π-bond order for the C—C is larger than the π-bond order for the C—O bond of the enolate anion derived from acetaldehyde. However, when a Me group is substituted on the α-C atom the π-bond order for the C—C bond decreases. The negative charge on the α-carbon also decreases, but most of this charge is withdrawn by the Me group and not transferred to the CO group. An alkyl group has little effect on the total negative charge on the terminal carbon when the alkyl group is substituted on the carbonyl C atom. It is not surprising that of the two possible enolate anions derived from methylethyl ketone the most substituted anion is calculated to be the more stable isomer. These calculations indicate that a Me group stabilizes negatively charged systems when the Me group is bonded to a negatively charged atom. This conclusion is not so startling in view of the results of the calculations on other carbanion systems.

However, these calculations should be viewed with caution when solution data are used to criticize the conclusions. After all the effects of the solvent and the counter-ion are neglected in the calculation. On the other hand, solution data should be used to interpret isolated molecule phenomena with extreme care, particularly since the magnitude of solvent effects can be considerable.

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