Electric Field Effects on the ^{13}C Chemical Shifts of Model Compounds

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Abstract: Using the SCF finite perturbation theory of ^{13}C chemical shifts at the INDO level of approximation, calculations have been carried out on ethane, ethylene, and acetylene systems subject to the fields generated by positive or negative monopoles or dipoles placed near the hydrocarbon frameworks in the calculations. Rather large effects of roughly equal magnitudes (up to about 7 ppm) have been obtained for the ethylene and acetylene systems, in qualitative agreement with known experimental patterns. Only small effects were found for the ethane system, implying an unfavorable prognosis for the use of electric field effects in conformational studies of saturated hydrocarbon frameworks, in contrast to the case for corresponding unsaturated cases. Some linear correlations are found between computed ^{13}C chemical shifts and pertinent electric field components. While some linear correlations are found between the shifts and computed electron density elements for specific related cases, completely general relationships of this type were not found. The results are discussed in terms of a simple bond polarization model, emphasizing the important role played by C–H polarizations in determining the geometrical dependences of the electric field effects.

Introduction

1. Background. The area of nuclear magnetic resonance as a tool for conformational analysis has become increasingly popular. Previously, this area was limited to analyzing proton spectra, but with the advent of more sophisticated instrumentation and techniques, allowing the routine acquisition of ^{13}C data, an extensive amount of work has been aimed at utilizing ^{13}C magnetic resonance as an aid to conformational analysis. This work has led to the identification of such conformationally dependent phenomena as the γ effect[1] and the δ effect.[2] Perhaps an equally promising phenomenon, which may have utility in conformational analysis by ^{13}C NMR, is the electric field effect.

Buckingham[3] was the first to suggest that polar groups in one part of a molecule could give rise to an electric field which would cause shifts in the shielding constants in another part of the molecule. In a theoretical treatment of this postulated electric field effect, Buckingham showed that the induced chemical shift should be proportional to the first power of the field. Horsley and Sternlicht[4] suggested that such an effect might exist for ^{13}C shielding constants in amino acids. More recently, Batchelor, Prestegard, Cushley, and Lipsky[5] performed a study on fatty acid systems, in which a large linear electric field effect was found to exist. The authors discussed this effect in terms of its geometrical dependence, with an eye toward utilizing it in conformational analysis by ^{13}C NMR. From the theoretical viewpoint, the direction and magnitude of the shifts were discussed in terms of bond polarizabilities and a correlation of electron density with chemical shift. At about the same time, Yonemoto[6,7] reported ^{13}C shifts in nitriles and alkenes which were interpreted in terms of a rather large electric field effect.

The purpose of the study reported here was to obtain theoretical guidelines regarding the effect that electrical monopoles and dipoles have on a set of simple hydrocarbon frameworks. The point of view of this work was primarily oriented toward ^{13}C shielding constants, but also explored was the effect of an electric field on electron densities and the relationship between these two dependences. A molecular orbital theory of shielding constants was utilized, and the results indicate that the theory reproduces, at least qualitatively, the experimentally known aspects of the electric field effect on ^{13}C shielding constants.

The results of this study also bear upon the general question of the relationship between electron density and chemical shifts. Evidence is presented which indicates that a linear relationship should not be expected in general, although in specific situations, covering only certain types of structural cases, such linear correlations can sometimes be found for certain electron density elements. The geometrical dependence of the electric field effect on ^{13}C shielding constants and electron distributions will also be discussed.

2. Calculations. The computational method is based on a modification of the original INDO-level, finite perturbation theory of shielding constants, reported by Ellis, Maciel, and McIver.[8] The modification consists of maintaining two-center angular momentum terms and dipole terms in the Hamiltonian, terms which were neglected in the theory in its original form.[9,10] Associated with these modifications was a need for different semiempirical atomic parameters[11] for carbon and hydrogen.[12] Reasons for making these modifications and a more detailed discussion of them can be found elsewhere.

The monopole and dipole electric fields were introduced into the calculation by means of using "modified" hydrogen centers as artificial monopoles (using two to form a dipole). These artificial monopoles were created by altering the values of $\frac{1}{2}(I + A)$ and β_0 for the appropriate hydrogen centers.[12] For instance, giving a hydrogen atom a large positive orbital energy ensures that it will not be populated by any electron density, thereby creating a positively charged center. In both cases, it is desirable to have the atoms being employed as artificial monopoles interacting covalently with the rest of the molecule as little as possible. This is accomplished by setting the β_0 for the hydrogen center representing the monopole to a large positive value. In the case of the negatively charged monopoles, a large Slater exponent is employed; this has the effect of shrinking the monopole's 1s orbital, creating the effect of a point charge. In generating a dipolar field, the two oppositely charged hydrogen monopoles were situated with a distance of 1.3 Å between them.

In a study of this kind it is, of course, desirable to carry out as complete a geometry variation as possible, i.e., to examine a large number of geometrical arrangements of the monopoles and dipoles relative to the hydrocarbon frameworks and to employ a representative set of hydrocarbon frameworks. Balancing these points against considerations involving computing time, it was decided to carry out a fairly detailed study of the angular dependence of monopoles and dipoles for a distance of 5 Å from the monopole or dipole to the center of the C–C bond, and a study of the distance dependence of negative monopoles oriented along the C–C axis. The molec-

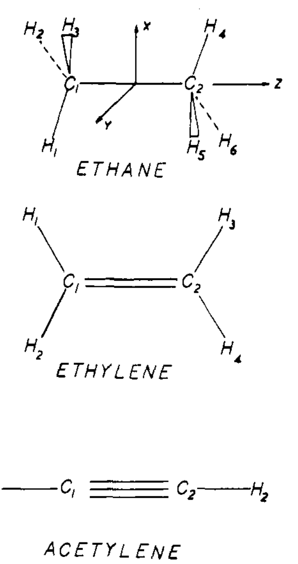


Figure 1. Orientations of ethane, ethylene, and acetylene with respect to a Cartesian coordinate system as actually employed in the calculations.

ular frameworks chosen for this study were ethane, ethylene, and acetylene. These systems are not only small, but they represent the main classes of carbon–carbon bonds. Standard geometries, as proposed by Pople and Gordon,[13] were used for the hydrocarbon frameworks in all calculations.

In the course of carrying out the modified INDO finite perturbation calculations of ^{13}C shielding constants reported in this paper, the density matrix is, of course, also obtained with each calculation. At the INDO level, the diagonal elements of the density matrix correspond to orbital populations (orbital electron densities). Some of these electron density elements have been presented in this paper. They are not meant to represent primary sources of information on electronic distributions in the systems studied, which would more appropriately be obtained by ab initio calculations, or even by the standard INDO or CNDO approaches. However, it is our position that the trends of the electron density patterns introduced by the electric field effects of this study are qualitatively correct as obtained by the modified INDO calculations. Some results are presented so that one can make qualitative comparisons of trends in the electron distributions with trends in computed ^{13}C shielding constants.

It should also be pointed out that the finite perturbation theory of ^{13}C chemical shifts has experienced an evolutionary improvement during the past few years, e.g., via improved parametrization and inclusion of previously neglected terms in the Hamiltonian matrix. Hence, it is likely that the results reported here can be improved upon during the next few years. Nevertheless, we believe that the important features of the results described here will not be overturned in future calculations using improved theoretical frameworks.

Results and Discussion

1. Computational Results. Figure 1 summarizes the orientations of the various molecules employed in the calculations, with respect to a Cartesian coordinate system, as well as the numbering of the atoms. Figure 2 presents the geometrical orientations of the monopoles and dipoles with respect to the carbon–carbon bond of interest; these orientations are referred to by number in the later tables. Tables I and II present the computed diamagnetic and paramagnetic contributions to the ^{13}C shielding constants of the acetylene and ethylene systems, respectively, in the presence of a monopole or dipole in a variety of orientations. Tables III and IV present the corresponding computed electron densities.

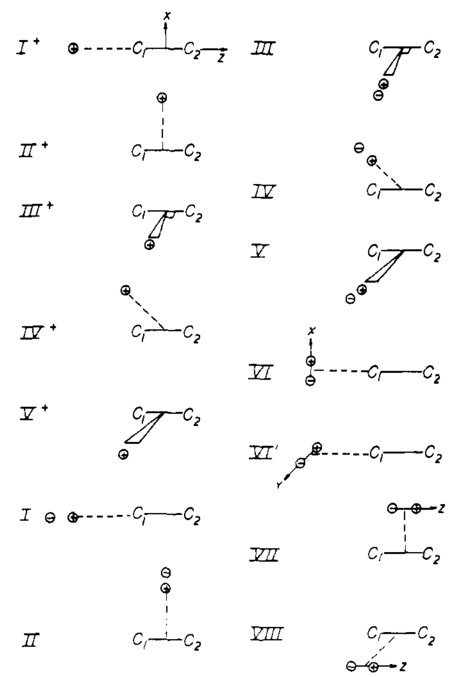


Figure 2. Configurations of monopoles and dipoles with respect to the hydrocarbons for which calculations were performed. Although not pictured here, calculations were performed for cases where a negative monopole replaces a positive monopole. Such configurations are noted in the text and tables with a minus superscript. Configurations where the sense of the dipole is reversed from that pictured here are noted with a prime superscript in the text and tables. θ is the angle between the C_1-C_2 axis and the dashed or wedged line.

2. Comparison of Theory with Experiment; Ethylene and Acetylene. From the point of view of the possible importance of electric field effects, unsaturated systems have been studied experimentally to a far greater extent than have saturated systems, and for this reason a comparison of calculated and experimental trends is limited initially here to only the acetylene and ethylene cases. There are three especially important comparisons to be made between theory and experiment, each of which will be discussed in turn. They are: (A) the magnitude of the induced shifts in the shielding constants; (B) the direction of the induced shifts in the shielding constants; and (C) whether the effect is linear with respect to the electric field.

A. Magnitude of the Shifts in ^{13}C Shielding Constants. As can be seen in Tables I and II, the magnitude of the shifts in the shielding constants are substantial. For the configurations studied, the absolute value of the difference in the shielding constants for the two carbons, C(1) and C(2), is as large as 14.2 ppm for the ethylene system and 12.3 ppm for the acetylene system. Both of these maximum values are obtained when monopoles are oriented along the molecular carbon–carbon axis. Such systems might be expected to bear a similarity to carboxylate or ammonium ions, although in real systems the geometrical configuration will generally vary with time. Electric field effects in neutral molecules can be expected to arise if polar groups are present, e.g., polar head groups, such as carboxylic acid and ester groups. The largest computed values found in Tables I and II for the differences between the shielding constants of the two carbons due to the presence of a dipole are 5.35 ppm for ethylene and 4.46 ppm for acetylene. These magnitudes are in good qualitative agreement with experimental data that have been attributed to electric field effects, although the calculated differences are somewhat larger than what have been reported experimentally. This is probably due to the fact that in reality the polar head groups in the experimental systems are conformationally mobile, and the ex-

Table I. Calculated[a] ^{13}C Shielding Constants for Acetylene System

Configuration[b]	$\sigma_d(C(1))$[c]	$\sigma_p(C(1))$[d]	$\sigma_T(C(1))$[e]	$\delta_{C_2H_2}(C(1))$[f]	$\sigma_d(C(2))$	$\sigma_p(C(2))$	$\sigma_T(C(2))$	$\delta_{C_2H_2}(C(2))$
Normal[g]	58.10	−138.45	−80.35	0.00	58.10	−138.45	−80.35	0.00
				Monopoles				
I+	58.20	−131.10	−72.90	7.45	57.78	−142.88	−85.10	−4.75
I−	57.97	−144.88	−86.91	−6.56	58.40	−133.01	−74.61	5.74
III+	58.13	−133.34	−80.21	0.14	58.13	−138.34	−80.21	0.14
III−	58.05	−137.55	−79.50	0.85	58.05	−137.55	−79.50	0.85
V+	58.26	−133.58	−75.32	5.03	57.88	−142.00	−84.12	−3.77
V−	57.92	−142.31	−84.39	−4.04	58.29	−133.94	−75.65	4.70
				Dipoles				
I	58.11	−135.22	−77.12	3.23	57.97	−139.64	−81.67	−1.32
I′	58.07	−140.62	−82.55	−2.20	58.21	−136.30	−78.09	2.26
III	58.11	−138.13	−80.02	0.33	58.11	−138.13	−80.02	0.03
III′	58.07	−137.75	−79.68	0.67	58.07	−137.75	−79.68	0.67
V	58.15	−136.29	−78.14	2.21	58.01	−139.45	−81.44	−1.09
V′	58.02	−139.55	−81.52	−1.17	58.17	−136.49	−78.32	2.03
VI	58.09	−137.98	−79.89	0.46	58.09	−137.91	−79.82	0.46
VIII	58.01	−139.41	−81.40	1.05	58.16	−136.47	−78.31	−2.04

[a] Calculated using the modified version of INDO finite perturbation theory of shielding constants described in the Introduction. [b] Roman numerals refer to configurations given in Figure 2; in all cases, the distance between the center of the carbon-carbon bond and the monopole or the center of the dipole is 5 Å. [c] σ_d is the calculated diamagnetic contribution to the shielding, in parts per million. The numbering of carbon atoms is specified in Figure 2. [d] σ_p is the calculated paramagnetic contribution to the shielding, in parts per million. [e] σ_T is the total shielding $= \sigma_p + \sigma_d$, in parts per million. [f] $\delta_{C_2H_2}$ is the computed shift with respect to normal acetylene, in parts per million. Larger value corresponds to higher shielding. σ_T(electric field) − σ_T(normal) = $\delta_{C_2H_2}$. [g] Results for acetylene in the absence of an electric field.

Table II. Calculated[a] ^{13}C Shielding Constants for Ethylene System

Configuration[b]	$\sigma_d(C(1))$[c]	$\sigma_p(C(1))$[d]	$\sigma_T(C(1))$[e]	$\delta_{C_2H_4}(C(1))$[f]	$\sigma_d(C(2))$	$\sigma_p(C(2))$	$\sigma_T(C(2))$	$\delta_{C_2H_4}(C(2))$
Normal[g]	57.80	−194.42	−136.62	0.00	57.80	−194.42	−136.62	0.00
				Monopoles				
I+	57.97	−187.62	−129.72	6.90	57.56	−201.36	−143.80	−7.18
I−	57.62	−201.28	−143.66	−7.04	58.04	−187.52	−129.48	7.14
II+	57.78	−194.50	−136.72	−0.10	57.78	−194.50	−136.72	−0.10
II−	57.82	−194.43	−136.61	0.01	57.82	−194.43	−136.61	0.01
III+	57.86	−194.31	−136.45	0.17	57.86	−194.31	−136.45	0.17
III−	57.74	−194.53	−136.79	−017	57.74	−194.53	−136.79	−0.17
IV+	57.86	−190.18	−132.32	4.30	57.65	−198.99	−141.34	−4.72
IV−	57.73	−199.01	−141.28	−4.66	57.95	−189.84	−131.89	−4.73
V+	57.98	−189.54	−131.56	5.05	57.65	−199.27	−141.62	−5.00
V−	57.62	−199.32	−141.70	−5.08	57.94	−189.62	−131.67	5.01
				Dipoles				
I	57.86	−191.86	−134.00	2.62	57.70	−197.03	−139.33	−2.71
I′	57.73	−196.99	−139.26	−2.64	57.90	−191.81	−133.91	2.71
II	57.79	−194.44	−136.65	−0.03	57.79	−194.44	−136.65	−0.03
II′	57.81	−194.41	−136.60	0.02	57.81	−194.41	−136.60	0.02
III	57.83	−194.37	−136.54	0.08	57.83	−194.37	−136.54	0.08
III′	57.77	−194.47	−136.70	−0.08	57.77	−194.47	−136.70	−0.08
IV	57.80	−192.89	−135.08	1.54	57.75	−196.07	−138.32	−1.70
IV′	57.79	−196.02	−138.23	−1.61	57.85	−192.77	−134.92	1.70
V	57.88	−192.48	−134.60	2.02	57.74	−196.33	−138.59	1.97
V′	57.72	−196.27	−138.55	−1.97	57.86	−192.61	−134.76	1.86
VI	57.80	−194.45	−136.65	−0.03	57.80	−194.42	−136.62	0.00
VI′	57.80	−194.42	−136.62	0.00	57.80	−194.42	−136.62	0.00
VII	57.77	−195.56	−138.19	−1.57	57.83	−192.90	−135.07	1.55
VIII	57.74	−196.16	−138.42	−1.80	57.86	−192.68	−134.82	1.80

[a] Calculated using the modified version of INDO finite perturbation theory of shielding constants described in the Introduction. [b] Roman numerals refer to configurations given in Figure 2; in all cases, the distance between the center of the carbon–carbon bond and the monopole or the center of the dipole is 5 Å. [c] σ_d is the calculated diamagnetic contribution to the shielding, in parts per million. The numbering of carbon atoms is specified in Figure 2. [d] σ_p is the calculated paramagnetic contribution to the shielding, in parts per million. [e] σ_T is the total calculated shielding $= \sigma_p + \sigma_d$, in parts per million. [f] $\delta_{C_2H_4}$ is the computed shift with respect to normal ethylene, in parts per million. Larger values correspond to higher shielding. σ_T(electric field) − σ_T(normal) = $\delta_{C_2H_4}$. [g] Results for ethylene in the absence of an electric field.

perimental result arises from a conformational averaging. Also it should be noted that the magnitude of the dipole moment of an actual head group is not nearly as large as those represented in the calculations presented here, and the average distance of a dipolar head group from a carbon–carbon bond of interest varies from system to system.

Table III. Calculated[a] Valence-Shell Electron Densities for Acetylene System

Configuration[b]	C(1))					C(2))						
	P_{2s2s}[c]	P_{xx}	P_{yy}	P_{zz}	P_{TOT}[d]	P_{2s2s}	P_{xx}	P_{yy}	P_{zz}	P_{TOT}	P_{ss}(H(1))	P_{ss}(H(2))
Normal[e]	1.1483	1.0000	1.000	0.9115	4.0598	1.1483	1.0000	1.0000	0.9115	4.0598	0.9402	0.9402
						Monopoles						
I+	1.1406	1.0206	1.0206	0.8893	4.0711	1.1543	0.9794	0.9794	0.9117	4.0248	0.9822	0.9218
I−	1.1642	0.9793	0.9793	0.9243	4.0471	1.1499	1.0207	1.0207	0.9026	4.0939	0.8995	0.9596
III+	1.1538	1.0000	1.0000	0.9100	4.0638	1.1538	1.0000	1.0000	0.9100	4.0638	0.9362	0.9362
III−	1.1500	1.0000	1.0000	0.9048	4.0548	1.1500	1.0000	1.0000	0.9048	4.0548	0.9452	0.9452
V+	1.1481	1.0149	1.0149	0.9077	4.0786	1.1543	0.9851	0.9851	0.9116	4.0361	0.9593	0.9260
V−	1.1560	0.9851	0.9851	0.9138	4.0400	1.1497	1.0149	1.0149	0.9029	4.0824	0.9221	0.9554
						Dipoles						
I	1.1464	1.0076	1.0076	0.8992	4.0608	1.1525	0.9924	0.9924	0.9087	4.0460	0.9591	0.9341
I′	1.1576	0.9924	0.9924	0.9154	4.0578	1.1513	1.0076	1.0076	0.9060	4.0725	0.9223	0.9473
III	1.1510	1.0000	1.0000	0.9062	4.0572	1.1510	1.0000	1.0000	0.9062	4.0572	0.9385	0.9385
III′	1.1528	1.0000	1.0000	0.9087	4.0615	1.1528	1.0000	1.0000	0.9087	4.0615	0.9429	0.9429
V	1.1505	1.0055	1.0055	0.9050	4.0665	1.1526	0.9945	0.9945	0.9088	4.0504	0.9475	0.9357
V′	1.1533	0.9945	0.9945	0.9098	4.0521	1.1512	1.0055	1.0055	0.9060	4.0682	0.9339	0.9457
VI	1.1519	1.0000	1.0000	0.9074	4.0593	1.1519	1.0000	1.0000	0.9074	4.0593	0.9407	0.9407
VIII	1.1526	0.9946	0.9946	0.9088	4.0506	1.1512	1.0054	1.0054	0.9060	4.0680	0.9358	0.9456

[a] Calculated using the modified version of INDO finite perturbation theory of shielding constants described in the Introduction. [b] Roman numerals refer to configurations given in Figure 2; in all cases, the distance between the center of the carbon–carbon bond and the monopole or the center of the dipole is 5 Å. The numbering of carbons is specified in Figure 2. [c] P_{2s2s} is an orbital electron density for the 2s orbital on carbon, given by: $P_{2s2s} = 2\Sigma_i^{occ}C_{2s_i}{}^*C_{2s_i}$. [d] P_{TOT} is the valence-shell electron density for carbon, given by: $P_{TOT} = P_{2s2s} + P_{xx} + P_{yy} + P_{zz}$. [e] Results for acetylene in the absence of an electric field.

Table IV. Calculated[a] Valence-Shell Electron Densities for Ethylene System

Configuration[b]	C(1)					C(2)					P_{ss}-(H(1))	P_{ss}-(H(2))	P_{ss}-(H(3))	P_{ss}-(H(4))
	P_{2s2s}[c]	P_{xx}	P_{yy}	P_{zz}	P_{TOT}[d]	P_{2s2s}	P_{xx}	P_{yy}	P_{zz}	P_{TOT}				
Normal[e]	1.0914	0.9532	1.000	0.9695	4.0141	1.0914	0.9532	1.000	0.9695	4.0141	0.9929	0.9929	0.9929	0.9929
						Monopoles								
I+	1.0875	0.9337	1.0433	0.9700	4.0345	1.0936	0.9683	0.9567	0.9669	3.9855	1.0119	1.0019	0.9781	0.9781
I−	1.0956	0.9727	0.9567	0.9686	3.9936	1.0897	0.9381	1.0434	0.9719	4.0431	0.9740	0.9740	1.0078	1.0078
II+	1.0911	0.9517	1.0000	0.9690	4.0118	1.0911	0.9517	1.0000	0.9690	4.0118	1.0144	0.9738	1.0144	0.9738
II−	1.0922	0.9542	1.0000	0.9700	4.0164	1.0922	0.9542	1.0000	0.9700	4.0164	0.9715	1.0121	0.9715	1.0121
III+	1.0932	0.9571	1.0000	0.9711	4.0214	1.0932	0.9571	1.0000	0.9711	4.0214	0.9893	0.9893	0.9893	0.9893
III−	1.0897	0.9493	1.0000	0.9679	4.0069	1.0897	0.9493	1.0000	0.9679	4.0069	0.9965	0.9965	0.9965	0.9965
IV+	1.0874	0.9356	1.0298	0.9684	4.0212	1.0935	0.9649	0.9702	0.9681	3.9967	1.0356	0.9838	0.9899	0.9728
IV−	1.0962	0.9701	0.9701	0.9704	4.0068	1.0896	0.9414	1.0299	0.9707	4.0316	0.9506	1.0020	0.9958	1.0131
V+	1.0904	0.9436	1.0300	0.9715	4.0355	1.0936	0.9651	0.9700	0.9684	3.9971	1.0024	1.0024	0.9814	0.9814
V−	1.0925	0.9628	0.9700	0.9674	3.9927	1.0894	0.9413	1.0300	0.9705	4.0312	0.9835	0.9835	1.0045	1.0045
						Dipoles								
I	1.0899	0.9458	1.0162	0.9697	4.0216	1.0920	0.9584	0.9838	0.9684	4.0026	1.0001	1.0001	0.9878	0.9878
I′	1.0930	0.9605	0.9838	0.9693	4.0066	1.0908	0.9479	1.0163	0.9706	4.0256	0.9858	0.9858	0.9981	0.9981
II	1.0912	0.9526	1.0000	0.9693	4.0131	1.0912	0.9526	1.0000	0.9693	4.0131	1.0007	0.9862	1.0007	0.9862
II′	1.0917	0.9537	1.0000	0.9697	4.0151	1.0917	0.9537	1.0000	0.9697	4.0151	0.9852	0.9996	0.9852	0.9996
III	1.0923	0.9551	1.0000	0.9703	4.0177	1.0923	0.9551	1.0000	0.9703	4.0177	0.9912	0.9912	0.9912	0.9912
III′	1.0906	0.9513	1.0000	0.9688	4.0107	1.0906	0.9513	1.0000	0.9688	4.0107	0.9947	0.9947	0.9947	0.9947
IV	1.0894	0.9457	1.0110	0.9687	4.0148	1.0921	0.9575	0.9890	0.9690	4.0076	1.0113	0.9888	0.9911	0.9861
IV′	1.0936	0.9605	0.9890	0.9703	4.0134	1.0907	0.9488	1.0110	0.9700	4.0205	0.9746	0.9970	0.9948	0.9997
V	1.0912	0.9500	1.0117	0.9705	4.0234	1.0922	0.9576	0.9883	0.9690	4.0071	0.9961	0.9961	0.9987	0.9987
V′	1.0916	0.9561	0.9989	0.9685	4.0051	1.0907	0.9490	1.0111	0.9700	4.0208	0.9900	0.9900	0.9970	0.9970
VI	1.0915	0.9531	1.0000	0.9695	4.0141	1.0914	0.9532	1.0000	0.9695	4.0141	1.0045	0.9814	.9955	0.9904
VI′	1.0914	0.9532	1.0000	0.9695	4.0141	1.0914	0.9532	1.0000	0.9695	4.0141	0.9929	9.9929	0.9929	0.9929
VII	1.0927	0.9587	0.9896	0.9696	4.0106	1.0901	0.9476	1.0105	0.9694	4.0176	0.9836	0.9915	1.0023	0.9944
VIII	1.0918	0.9566	0.9895	0.9688	4.0067	1.0910	0.9498	1.0106	0.9702	4.0216	0.9896	0.9896	0.9963	0.9963

[a] Calculated using the modified version of INDO finite perturbation theory of shielding constants described in the Introduction. [b] Roman numerals refers to configurations given in Figure 2; in all cases, the distance between the center of the carbon–carbon bond and the monopole or the center of the dipole is 5 Å. The numbering of carbons is specified in Figure 2. [c] P_{2s2s} is an orbital electron density for the 2s orbital on carbon, given by: $P_{2s2s} = 2\Sigma_i^{occ}C_{2s_i}{}^*C_{2s_i}$. [d] P_{TOT} is the valence-shell electron density for carbon, given by: $P_{TOT} = P_{2s2s} + P_{xx} + P_{yy} + P_{zz}$. [e] Results for ethylene in the absence of an electric field.

Batchelor et al.[5] noted that the magnitude of the electric field effect on ^{13}C shifts for double bonds was about the same as for triple bonds. Tables I and II indicate that the computational theory employed here shows the same general result, although we actually observe an effect which is about 15–20% smaller for the acetylene system.

The electric field effects on the shielding constants in the ethane system are found to be an order of magnitude smaller than those for the ethylene or acetylene systems.[12] This pattern is also in agreement with experimental indications. The ethane results are discussed in a later section.

B. Direction of the Shifts. Experimentally it is found that for two adjacent unsaturated carbon atoms, the shielding constants are shifted in opposite directions by an electric field. In the case of doubly bonded carbons, the experimental shifts are equal in magnitude (relative to an analogous system with the field absent) and opposite in direction when the polar head group is five or more bonds away. Yonemoto's data[6,7] indicate that the shifts are not equal in magnitude when the polar head group is only one bond away; this may be due to a nonuniform field and/or effects other than those described simply as a through-space electric field effect (through-bond effects). The calculated results are in qualitative agreement with the experimental data obtained for a head group five bonds or more away from the carbon-carbon bond of interest. The only exception in the calculated results in terms of the shifting of the two carbon shieldings in opposite directions occurs when a monopole or dipole is oriented perpendicular to the carbon-carbon bond, (e.g., orientation II). In these cases, the shieldings of both carbons are shifted in the same direction, a result dictated by symmetry. It should also be noted that, although the two calculated ^{13}C shielding constants for the acetylene system are shifted in opposite directions when the monopole or dipole lies along the C-C axis, the magnitudes of the two shifts are not equal.

Considering conformations I$^+$ and I of Figure 2, the calculated ^{13}C shielding constants for C(1) in ethylene and acetylene are always shifted to less negative values, while those for C(2) are consistently shifted to more negative values. If the sign of the monopole is reversed (configuration I$^-$) or the sense of the dipole is reversed (configuration I′), then the shifts in the ^{13}C shielding constants of the acetylene and ethylene systems above are also reversed in direction. These results also apply to the cases where the dipole or monopole is oriented at a 45° angle to the carbon-carbon bond, configurations IV$^+$, IV$^-$, V$^+$, V$^-$, IV, IV′, V, and V′, for acetylene and ethylene. This is in accord with the interpretations of experimentally obtained data.[5-7]

It should be noted that, where the monopole or dipole is oriented perpendicular to the carbon-carbon bond in ethylene (configurations II$^+$, II$^-$, III$^+$, III$^-$, II, II′, III, and III′) and the signs of the charges are reversed, the direction of the shift is reversed. Such is not the case for acetylene; no matter what the charge of the monopole, or the sense of the dipole, the ^{13}C shielding constants are always shifted to less negative values.

C. Linear Field Effect. As mentioned above, earlier theoretical[3] and experimental[5] work on the electric field effect has indicated the possible existence of a linear relationship between the magnitude of the field along the carbon-carbon bond of interest and the resulting shifts in the ^{13}C shielding constants. To conclude that a linear field effect obtains, two gross patterns are expected in the results. They are: (i) the magnitudes of the shifts in the ^{13}C shielding constants must fall off with the magnitude of the electric field component along the carbon-carbon bond; and (ii) the direction of the shifts in the ^{13}C shielding constants should reverse when the sign of the monopole or the sense of the dipole is reversed. As the latter behavior has been established above, it remains then to explore the calculated results to see whether the former is fulfilled.

The most straightforward and complete way to explore the existence of condition i would be to carry out a study of each of the various configurations shown in Figure 2, varying the distance (R) between the dipole or monopole and the center of the carbon-carbon bond of interest. We limited our distance-dependence study to configuration I$^-$, employing the ethane, ethylene, and acetylene systems and R values of 5.0, 5.47, 7.47, and 9.47 Å for the ethane system, 5.0, 5.66, 7.66, and 9.66 Å for the ethylene system, and 5.0, 5.8, 7.8, and 9.8 Å for the acetylene system. Of course, the other calculations summarized in Tables I and the analogous ones for ethane[12] also bear upon this point. The electric fields generated by the dipoles are smaller in magnitude than the fields generated by monopoles having the analogous geometrical orientations relative to the C-C bond of interest. Furthermore, a monopole or dipole which is not oriented along the carbon-carbon bond axis generates a field component that is weaker by a factor, cos θ (where θ is defined in Figure 2), than it would generate were it situated on the carbon-carbon axis. These situations are pictorially represented in Figure 3, along with the computed values of the electric field components along the carbon-carbon bond axis at the center of that bond. Part A of that figure depicts the systems in which the distance of a negative monopole from the center of the carbon-carbon bond was varied in order to vary the magnitude of the field at the center of the bond. Comparison of part B of Figure 3 with the 5-Å case in part A and comparison of part C with D shows the effect on the magnitude of the electric field at the center of the carbon-carbon bond when one replaces a monopole with a dipole. Comparison of Figure 3C with the 5-Å case in part A and of part D with B shows the effect on the magnitude of the pertinent electric field component at the center of the carbon-carbon bond when a monopole or dipole is oriented at $\theta = 45°$, rather than $\theta = 0°$. The cases shown in Figure 3 represent the pertinent configurations for which calculations were actually performed, relevant to the dependence of the shifts induced by the electric fields on the magnitudes of the fields.

Plots of the differences in the ^{13}C shielding constants, $\sigma_T(C(1)) - \sigma_T(C(2))$, vs. the magnitudes of the electric field components along the carbon-carbon bond at its center are presented in Figures 4 and 5 for the ethylene and acetylene cases, respectively. Only cases with negative monopoles or dipoles in which the negative end is closest to the hydrocarbon are included in the plots. These graphs indicate a rather strong linear dependence. When considered along with the results from section 2**B**, these results point strongly toward a linear field effect on ^{13}C shielding constants, which is in agreement with previous conclusions based on theoretical and experimental results.

The results from section 2 indicate that the theory does indeed reproduce, at least in a qualitative fashion, the most important features previously suggested for the electric field effect on ^{13}C shielding constants, based upon experiments and simple theoretical models. This lends confidence to other results obtained from the calculations, discussed below, which have not, or cannot, be obtained experimentally.

3. The Electronic Distributions. A. Flow of Electron Density in the Ethylene and Acetylene Systems. Previous discussions[4,5] of the electric field effect on ^{13}C shielding constants feature the suggestion that bond polarizability has an important direct bearing on how large an effect will be observed. Related to this is the popular assumption that the magnitude and direction of the shifts in ^{13}C shielding constants are simply related with changes in electron density. The basic assumption that has been made, an assumption that CNDO calculations[5] have to some degree confirmed for systems involving carbon-carbon double bonds affected by electric fields, is that there is a linear relationship between the polarization of a carbon-carbon double bond and the strength of the electric field component along the bond. Several empirical equations have been suggested which directly relate bond polarizability and changes in electron density with changes in ^{13}C shielding constants. Apparently the most successful of these approaches was that proposed by Horsley and Sternlicht;[4] their equation for the effect of an electric field on the ^{13}C shielding constants, $\Delta\sigma_C$, is

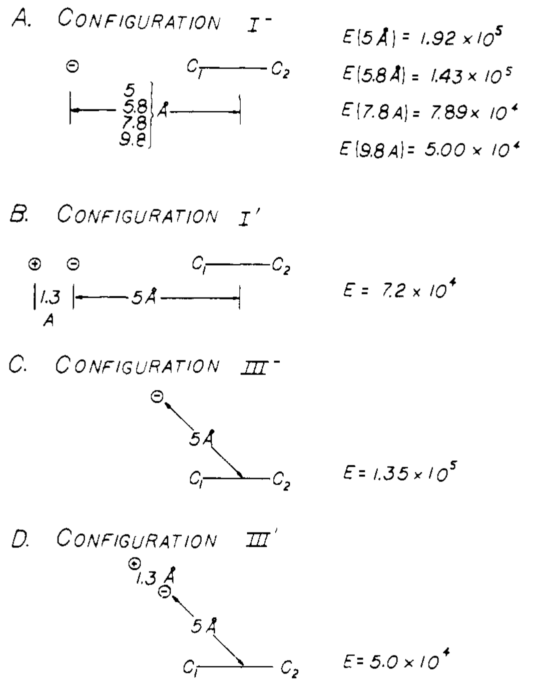


Figure 3. Some specific configurations of monopoles and dipoles, as well as the calculated electric field component (E) at the center of the carbon-carbon bond and along the bond axis (axial field component), for each case.

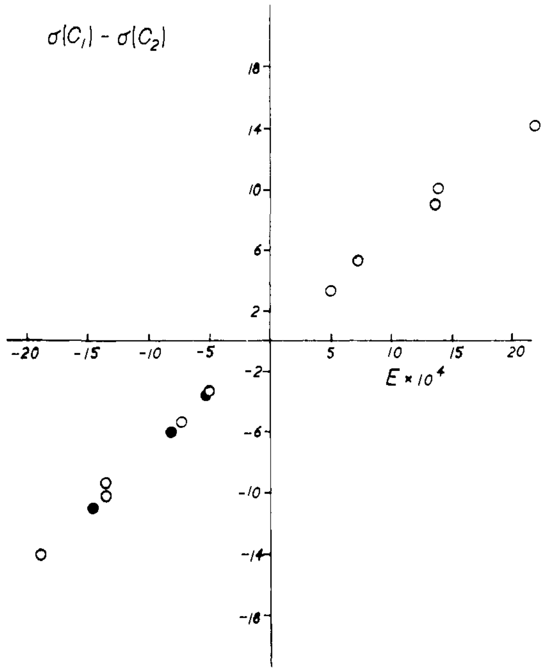


Figure 4. Plot of difference in computed ^{13}C chemical shifts for C(1) and C(2) ($\sigma(C(1)) - \sigma(C(2))$) vs. the axial electric field component at the center of the carbon-carbon bond (E) for the ethylene system. Black dots for this and all succeeding plots represent points for monopoles located at distances of >5 Å from the center of the carbon-carbon bond.

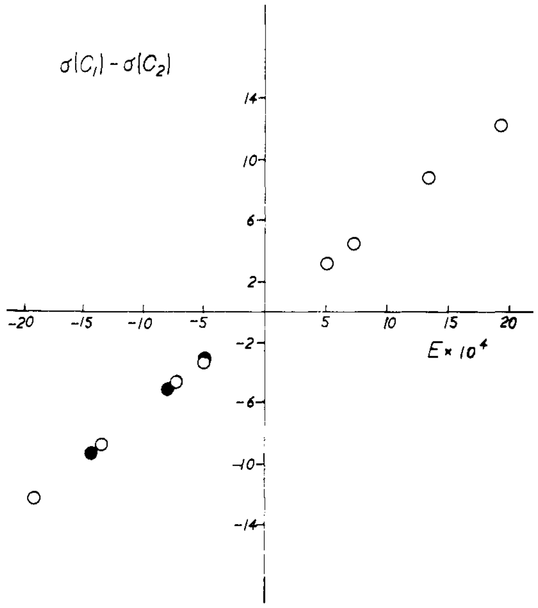


Figure 5. Plot of difference in computed ^{13}C chemical shifts for C(1) and C(2) ($\sigma(C(1)) - \sigma(C(2))$) vs. the axial electric field component at the center of the carbon-carbon bond (E) for the acetylene system.

$$\Delta\sigma_C = \frac{200 b_{\parallel}{}^{C} E_{\parallel} \times 10^{-6}}{|e| R_{C\text{-}C}} \tag{1}$$

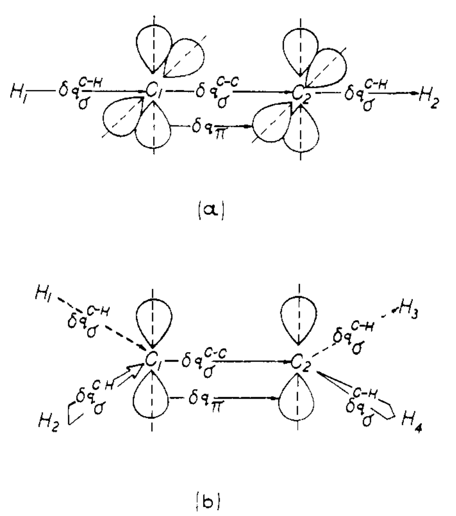
In this equation $b_{\parallel}{}^{C}$ is the bond polarizability of a carbon-carbon bond along its axis, $E_{\parallel}$ is the component of the electric field along the carbon-carbon bond axis, $R_{C\text{-}C}$ is the carbon-carbon bond length, $|e|$ is the magnitude of the charge of an electron, and the factor 200×10^{-6} is an estimate of the proportionality constant for an assumed linear relationship between the ^{13}C chemical shift and carbon electron density. Batchelor et al.[5] employed a CNDO calculation on a *cis*-2-butene system, artifically creating point charges at various distances along the carbon-carbon axis; they found a linear dependence between the strength of the field and the change in electron density on the carbon atoms in the double bond.

There are several points which indicate that rationalizations of electric field effects on ^{13}C shifts strictly in terms of carbon-carbon bond polarizabilities and electron densities may be considerably oversimplified. Perhaps the most important is the experimental fact that carbon-carbon triple bonds, although having a larger bond polarizability than carbon-carbon double bonds, do not exhibit a larger electric field effect. Also, as discussed below, it appears that the role of C-H bond polarizations may be very important, and the geometrical arrangements of these bonds may effect this role in an important manner.

Let us consider the changes in valence-shell electron density patterns promoted in the acetylene system by the electric fields. There are several trends which become readily apparent upon examining the carbon electron density patterns given in Table III. For cases in which the monopoles or dipoles are located along the carbon-carbon axis, we find the following trends in electron density: (a) The π-orbital electron density of C(1) is always shifted an equal amount and in the opposite direction from the π-orbital electron density of C(2). Mathematically, this can be expressed in terms of the equation

$$\delta p_{xx}(C(1)) = \delta p_{yy}(C(1)) = -\delta p_{xx}(C(2)) = -\delta p_{yy}(C(2)) \tag{2}$$

$\delta p_{xx}(C(1))$ is the change in electron density in the $2p_x$ orbital on C(1) for acetylene in the presence of a monopole or dipole, with respect to normal acetylene. (b) The total change in σ-electron density on a particular carbon atom is always in the opposite direction to the change in π density. Furthermore, the change in σ-electron density on C(1) is always opposite in sign to the change in σ-electron density on C(2) and is always larger in magnitude. (c) The change in the total valence-shell electron density on C(2) is generally greater than that on C(1). (d) The change in the π-electron density on a particular carbon atom is always far greater in magnitude than the change in the total σ-electron density.



(a)

(b)

Figure 6. A pictorial representation of the changes in electronic distribution in acetylene (a) and ethylene (b). δ_q represents changes in electron density, the direction of the changes being indicated by the arrows.

None of these four patterns applies to cases in which the monopole or dipole is oriented perpendicular to the carbon-carbon bond axis; these cases will be discussed separately. All the above-mentioned trends are also present, albeit diminished, when the monopole or dipole is oriented at a 45° angle relative to the carbon-carbon axis.

The four trends listed above present an interesting, although not surprising, picture of the influence of an electric field on the acetylenic system. As a representative case, Figure 6a presents a pictorial description of the flow of electronic density in the acetylene system when a negative monopole is oriented along the C-C bond axis. As can be deduced from Figure 6a and Table III (entry I^-), π- and σ-electron density flows from C(1) toward C(2). These changes in σ-electron density for C(1) and C(2) are more than compensated for by the flow of σ-electron density through the C-H bonds; electron density flows toward C(1) through the H(1)-C(1) bond and away from C(2) through the H(2)-C(2) bond. The net effect from the simultaneous polarization of the three bonds is an apparent opposition of σ- and π-electron density effects on the carbon atoms.

The fact that the change in total electron density on C(2) is always larger than on C(1) is due to the fact that the change in π-electron density on both carbons is of the same magnitude, but the change in σ-electron density on C(2), which is opposite in direction to the change in π-electron density on C(2), is less than that on C(1). These nonequivalent changes in σ-electron density on C(1) and C(2) arise from the nonequivalent effect that the electric field has on the two C-H bonds. Within the framework of a bond polarizability model (an admittedly oversimplified view) we assume that the change in σ-electron density on C(1) and C(2) due to a transfer between the two carbons is equal in magnitude and opposite in direction for the two carbons, just as is found for the π density on the two carbons. Equal effects on C(1) and C(2) do not result from the transfer of electron density through the C-H bonds, since the electric field will be stronger at the center of the C(1)-H(1) bond than at the center of the C(2)-H(2) bond. (See the hydrogen electron densities in Table III.) Thus, we see a larger overall change in σ-electron density on C(1) and a smaller change in total electron density.

The results for the ethylene system, summarized in Table IV and shown pictorially in Figure 6b, exhibit the same general features as those described for acetylene, but with some differences. The most significant patterns found for the ethylene system, under the influence of a monopole or dipole not oriented perpendicular to the carbon-carbon axis, are: (a) As with acetylene, the π-orbital electron density on C(1) is shifted an equal amount and in the opposite direction from the shift in the π-orbital electron density on C(2); i.e.,

$$\delta p_{yy}(\mathrm{C}(1)) = -\delta p_{yy}(\mathrm{C}(2)) \tag{3}$$

where the terms are as defined for eq 2. (b) As with acetylene, the total change in σ-electron density on a particular carbon atom is in the opposite direction to the change in the corresponding π density. Also, the change in σ-electron density on C(1) is always opposite to the change in σ-electron density on C(2). (c) The largest change in σ-electron density for the ethylene system occurs in the p_x orbital, which is the orbital most directly involved in the C-H bonds. (d) Unlike what was found for the acetylene case, the change in the total σ-electron density on C(1) is not always greater than on C(2) (cases V^+, V^-, V, V′). (e) The change in the total π-electron density for the ethylene system is comparable to that for acetylene in corresponding situations, even though there are two π-type p orbitals for each carbon of acetylene and only one for ethylene. (f) The change in the total σ-electron density of a carbon atom of the ethylene system is always smaller than for the corresponding acetylene system on C(1), and always larger for the ethylene case on C(2).

As represented pictorially in Figure 6b, the electron distribution in the ethylene system in which a negative monopole is oriented along the carbon-carbon bond axis behaves in an analogous manner to what was discussed above for the acetylene case (Figure 6a). Both the σ and π parts of the C-C bonding are polarized such that σ and π densities flow away from C(1) and toward C(2), while the flow of electron density in the C-H bonds is always in a direction which tends to oppose the net effects on carbon of electronic polarization of the C-C bonds.

The largest single difference between the ethylene and acetylene systems of this study is the orientation of the hydrogen atoms and C-H bonds with respect to the source of the electric field. The component of an electric field along a bond axis is governed by the cosine relationship mentioned above. For the specific cases shown in Figure 6, the component of the electric field along the C(1)-H(1) bond of ethylene is weaker than the component of the field along the C(1)-H(1) bond of acetylene, i.e., 1.14×10^5 esu at the center of the C(1)-H(1) bond of ethylene and 3.22×10^5 esu at the center of the C(1)-H(1) bond of acetylene. Of course, for ethylene, one must also consider the effect of the field on the C(1)-H(2) bond. This combination could, at most, double the effect of the C(1)-H(1) bond polarization on the σ-electron density at C(1). The fact that the field component quoted above for the C(1)-H(1) bond of ethylene is less than half of that for acetylene is consistent with the fact that larger H(1)-C(1) polarization effects are found at C(1) in acetylene than in ethylene. If one brings the same considerations to bear on the C(2)-H bonds of the acetylene and ethylene systems, it is found that the electric field component along the bond and at its center is 0.76×10^5 esu for the ethylene system and 1.27×10^5 esu for the acetylene system. In this case the field for ethylene is more than half the value for acetylene; thus, taking into account the number of relevant C(2)-H bonds, the total C-H polarization effect at C(2) in ethylene might be expected to exceed that for C(2) in acetylene. Indeed, the computed results in Tables III and IV show larger σ effects on C(2) for ethylene than for acetylene.

From the above discussion, one would be led to believe that the flow of electron density in these systems could be explained to a reasonable approximation in terms of a simple bond-polarization model, i.e., in terms of bond polarizabilities and the magnitudes and directions of the electric field components along individual bonds. Although this is usually the case, there

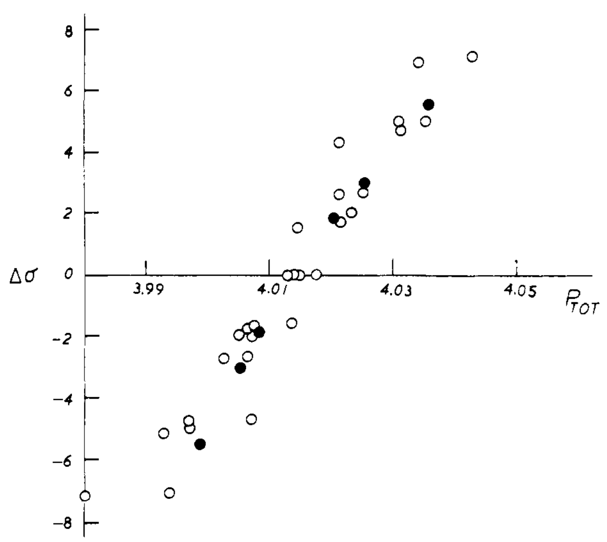


Figure 7. Plot of computed ^{13}C chemical shifts for C(1) and C(2) of the ethylene system induced by the electric fields ($\Delta\sigma = \sigma - \sigma_0$, where σ_0 is the shielding of normal ethylene) vs. the corresponding computed valence-shell electron densities (P_{TOT}) for those carbons.

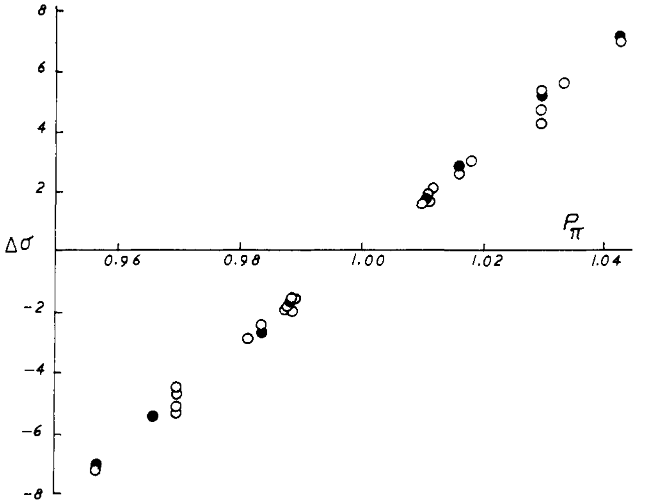


Figure 8. Plot of computed ^{13}C chemical shifts for C(1) and C(2) of the ethylene system induced by electric fields ($\Delta\sigma = \sigma - \sigma_0$, where σ_0 is the shielding of normal ethylene) vs. the corresponding computed π-electron density (P_π) for those carbons.

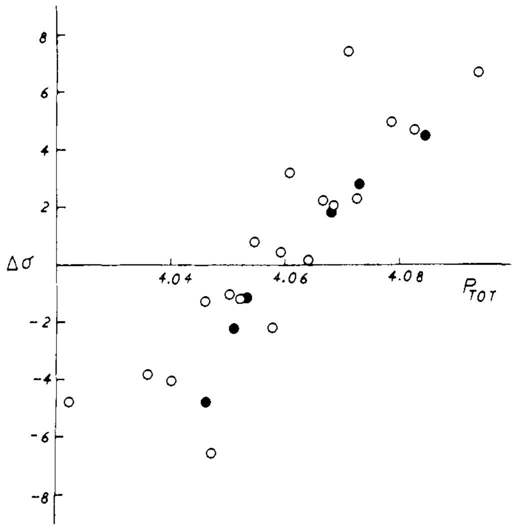


Figure 9. Plot of computed ^{13}C chemical shifts for C(1) and C(2) of the acetylene system induced by electric fields ($\Delta\sigma = \sigma - \sigma_0$, where σ_0 is the shielding of normal acetylene) vs. the corresponding computed valence-shell electron densities (P_{TOT}) for those carbons.

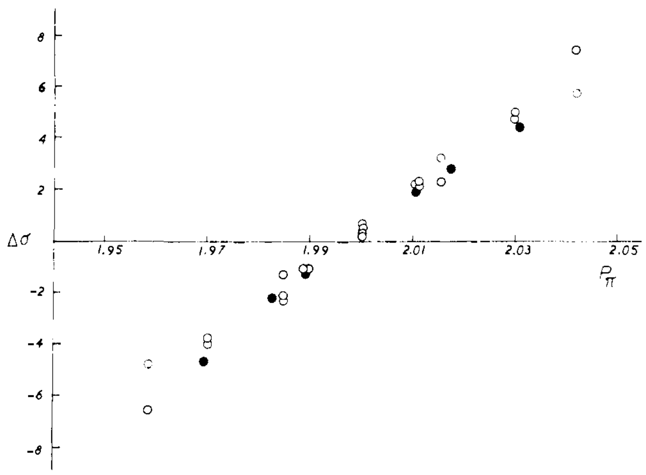


Figure 10. Plot of computed ^{13}C chemical shifts for C(1) and C(2) of the acetylene system induced by electric fields ($\Delta\sigma = \sigma - \sigma_0$, where σ_0 is the shielding of normal acetylene) vs. the corresponding computed π-electron densities (P_π) for these carbons.

are examples for ethylene, e.g., cases V^+, V^-, V, V′, where such a simple view is not adequate. We have already noted above that changes in σ-electron density on C(2) are larger than on C(1) for these cases, in direct contrast with all other cases discussed in this section. If one considers the V^- case, focusing on the relationship between the electric field and the orientation of the C(1)-H(1) bond, it would be predicted that electron density would flow from C(1) to H(1) by a simple C(1)-H(1) bond polarization. It should be noted that the electric field component along this bond and at its center is rather weak. Nevertheless, we find from Table IV that electron density is lost on H(1) (relative to its value on normal ethylene). A possible explanation for this behavior is that a partial positive charge at C(1) is created by the polarization of the C(1)-C(2) bond, which would tend to be compensated for by electron density flowing from H(1) to C(1) through the σ bond. It may be that this compensation overwhelms the rather weak effect of the electric field along the H(1)-C(1) bond.

It should be noted that when a dipole or monopole is oriented at a 45° angle to the molecular axis of ethylene, it is important to distinguish between the cases in which the monopole or dipole lies in the *xz* or *yz* plane. This distinction is not appreciably important as far as the π-electron flow is concerned (Table IV), but when the monopole or dipole is oriented in the *xz* plane, larger σ effects are observed (Table IV). This is due to the fact that the electric field component along the C(1)-H(1) bond is larger by a sizable amount in *xz* case relative to the *yz* case, which will lead to a larger polarization of the electron density in the C(1)-H(1) bond.

B. Changes in the Electron Density vs. Shifts in ^{13}C Shielding Constants. Figures 7 and 8 present plots of the shifts in the computed ^{13}C shielding constants, relative to the normal hydrocarbons, vs. the total and π-electron densities, respectively, for the ethylene system. Figures 9 and 10 present similar plots for the acetylene system. All of the results in Tables I-IV are included in these plots.

There are some interesting patterns which are made evident by studying Figures 7-10. Considering the plots of the ^{13}C shifts vs. the total electron density for the ethylene and acetylene systems (Figures 7 and 9), the strongest statement one can make is that there is a tendency toward higher shielding with an increase in the total electron density. However, these rough correlations by no means constitute simple linear relationships. If we now consider Figures 8 and 10 we find a quite

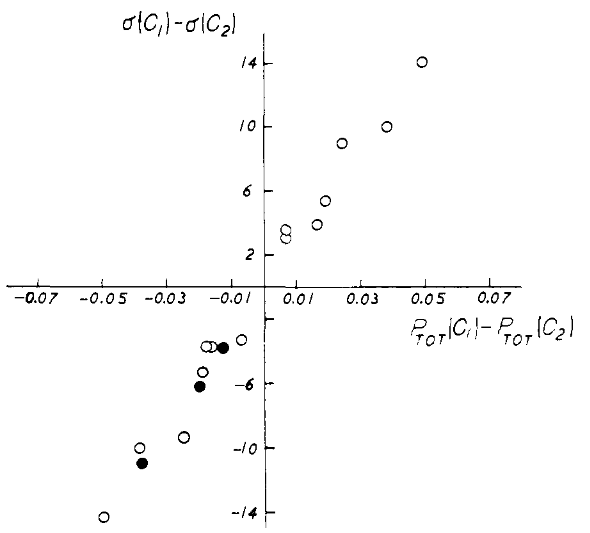


Figure 11. Plot of difference in computed ^{13}C chemical shifts for C(1) and C(2) (σ(C(1)) − σ(C(2)) vs. the corresponding difference in the computed total valence-shell electron densities for those carbons (P_{TOT}(C(1)) − P_{TOT}(C(2)) for the ethylene system.

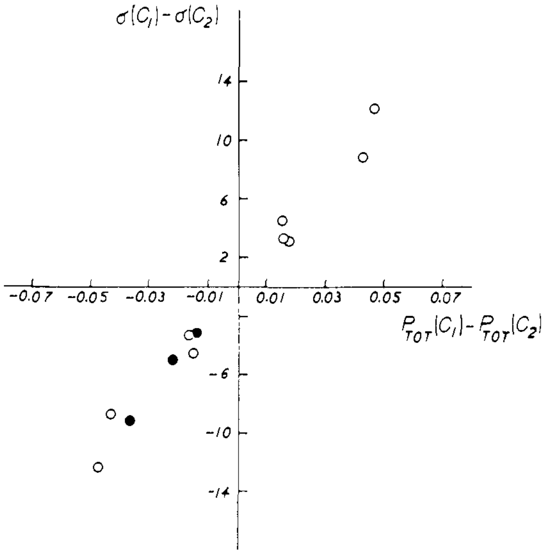


Figure 12. Plot of the difference in the computed ^{13}C chemical shifts for C(1) and C(2) (σ(C(1)) − σ(C(2)) vs. the difference in the computed valence-shell electron densities for those carbons for the acetylene system.

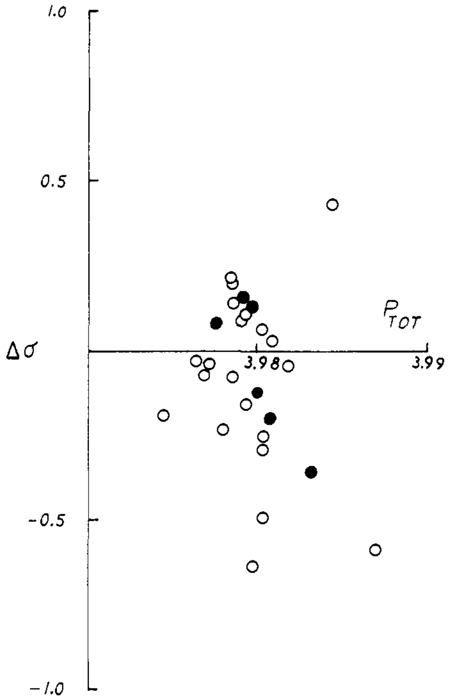


Figure 13. Plot of the computed ^{13}C chemical shifts induced by electric fields ($\Delta\sigma = \sigma - \sigma_0$, where σ_0 is the shift of normal ethane) vs. the computed valence-shell electron density (P_{TOT}) for the ethane system.

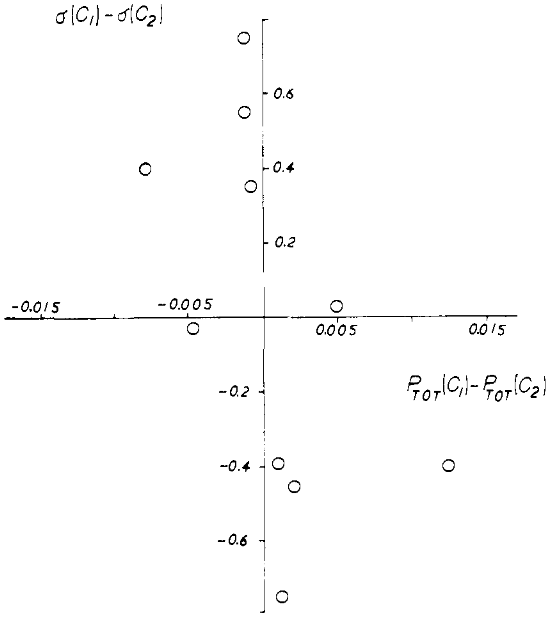


Figure 14. Plot of the difference in the computed ^{13}C chemical shifts for C(1) and C(2) (σ(C(1)) − σ(C(2)) vs. the difference in the computed valence-shell electron densities (P_{TOT}(C(1)) − P_{TOT}(C(2)) for the ethane system.

different situation. For both the acetylene and ethylene systems there appears to be nearly linear relationships between ^{13}C shifts and π-electron densities; the quality of the correlation is especially evident for the ethylene system.

Figures 11 and 12 present plots of the difference in the ^{13}C shielding constants vs. the difference in total electron density on C(1) and C(2) for the ethylene and acetylene systems, respectively. A comparison of these figures with Figures 7 and 9 indicates a more nearly linear relationship for these difference plots. Apparently, in taking these differences, certain features of the electric field effect upon the ^{13}C shielding constants and electron densities which are not accounted for by a simple linear correlation are eliminated in some manner. What the nature of these features may be cannot be readily determined at present.

The linear relationships discussed in this section represent examples of the interesting circumstance that, under certain limiting conditions for a particular set of closely related molecular systems, it is sometimes possible to find linear relationships between ^{13}C shifts and carbon electron density elements. It is, in general, difficult if not impossible to predict such cases without first carrying out diagnostic calculations. We consider it dangerous to assume the existence of linear correlations without supporting theoretical information.

C. Monopoles and Dipoles Oriented Perpendicular to the Carbon–Carbon Bond Axis. For orientations of the monopole or dipole along an axis which bisects the carbon–carbon bond axis (configuration III$^+$, III$^-$, III, III′, IV$^+$, IV, and IV′), the pattern of results is quite different from those of the other orientations discussed above. The most significant of these results are: (a) Because of the symmetry requirements, the ^{13}C shielding constants for both C(1) and C(2) are always shifted in the same direction and by the same magnitude. (b) The π-electron densities for the acetylene and ethylene systems remain unaltered. This is because there is no component of the field along the C–C bond. (c) If the sign of the monopole or the sense of the dipole is reversed, then the shifts in carbon electron density, relative to the normal hydrocarbon, change direction; for the ethylene system the shifts in ^{13}C shielding constants also change sign. (d) The acetylene system, on the other hand, is quite different. No matter what the sign of the monopole or the sense of the dipole, the shielding constants are always shifted to larger values even though the direction of the electron density changes depends upon the sign of the monopole or the sense of the dipole. (e) The magnitudes of the electric field effects for those orientations are much smaller than for any of the other orientations explored. This is because the effects that the electric fields exert on these systems are manifested only in the σ-electron networks. The reason that effects are exerted in the σ-electron network is that there is a component of the field along the C–H bonds; therefore, there is a polarization which takes place involving only σ bonds.

4. The Ethane System. The ethane system shows very little similarity to the ethylene and acetylene systems in its response to the presence of a dipole or monopole. Perhaps the most important result found for ethane[12] is the rather small magnitude of the effect the electric field has on the ^{13}C shielding constants. Most of the shielding constants are shifted 0.5 ppm or less. Part of this is due to the lower carbon–carbon bond polarizability for a single bond, but the shifts are so much smaller for the ethane system than for corresponding situations for ethylene and acetylene that bond polarizabilities cannot totally explain it.

The results acquired for monopoles and dipoles situated at 5 Å from the center of the carbon–carbon bond[12] suggest that there is no apparent correlation between changes in the valence-shell electron density of carbon and shifts in the ^{13}C shielding constants for the ethane system. This is graphically displayed in Figure 13. In all these ethane configurations, the computed electron density results show that the electron density flows in a manner analogous to what was discussed above for the ethylene and acetylene systems, a manner dictated by the position and sign of the source of the electric field, and by the orientation of the C–H bonds. However, the ^{13}C shielding constants for C(1) and C(2) shift in opposite directions in some cases, and in the same direction in other cases, relative to the shielding of unperturbed ethane. This is despite the fact that in all cases the electron densities of C(1) and C(2) are shifted in opposite directions.

Figure 14 presents a plot of the difference between the shifts in electron density for C(1) and C(2) vs. the difference in their ^{13}C shielding constants. Unlike the ethylene and acetylene cases, the data points in this figure do not indicate a narrower scatter than is found in Figure 13. The results obtained as a function of the distance R show that as the magnitude of the electric field is decreased by moving a negative monopole further out along the C–C bond axis, shifts in the shielding constants for the two carbons are always in opposite directions, and the magnitudes of the shift differences drop off with the magnitude of the field. It is clear that the ethane system is a far more complicated case. Its pattern of results reflects the absence of π-electron effects, which tend to dominate the responses of the ethylene and acetylene systems to the presence of a monopole or dipole, and the more complex array of C–H orientations.

It appears from these results that the ^{13}C chemical shifts of saturated carbon frameworks may not be very promising for observing or interpreting electric field effects. The results indicate that when the source of the field is at distances of greater than 5 Å, the effects are likely to be very small. At distances of 5 Å or less the effects may be larger, but they are difficult to interpret.

Summary and Conclusions

The modified INDO finite perturbation theory of ^{13}C shielding constants has been shown to account qualitatively for the known features of electric field effects on ^{13}C chemical shifts. Rather large effects of roughly equal magnitudes have been computed for ethylene and acetylene systems subjected to the influence of a monopole or dipole. Plots between differences in the ^{13}C shieldings of the two carbons of ethylene or acetylene vs. pertinent electric field components are found to be linear. Only small electric field effects have been found for the ethane system.

The geometrical dependences of electric field effects have been explored, and indicate promise for the future use of ^{13}C shift measurements on unsaturated carbons in conformational studies. However, the small size of the effects found in the calculations on the ethane system imply that such experimental conformational studies on saturated systems are not promising. The present results, and others that could be obtained by the same general methods, should prove useful in the interpretation of solvent effects on ^{13}C chemical shifts.

Examination of the density matrices obtained in this study indicate that, for most cases, sensible interpretations of the electric field effects on electronic distributions can be made on the basis of σ and π bond polarization models. These interpretations emphasize the important role played by C–H polarizations in determining the responses of these systems to an applied electric field.

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Supplementary Material Available: Tables A–H, parameters and constants for C and H (13 pages). Ordering information is given on any current masthead page.

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