dition of allenyl magnesium bromide to 1-bromo-2-butyne.[29]

The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England) of the type described by Turner.[30]

**Acknowledgment.** This work was supported by the Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, and by the Otto Röhm Stiftung.

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# $^1H$ and $^{13}C$ Nuclear Magnetic Resonance Spectra of Heteroaromatic Carbocations. Xanthylium Ions

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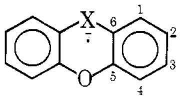
*Received December 16, 1974*

**Abstract:** The $^{13}C$ NMR spectra of highly stable xanthylium derivatives were measured and completely assigned with the use of double resonance technique and chemical shift criteria. The observed shifts, correlated with the total charge density calculated from CNDO, show an extensive delocalization of the positive charge.

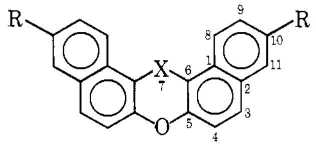
The aryl carbonium ions are the best investigated carbonium ions. Their structures have been determined by a variety of spectroscopic methods.[2] In contrast, few data are available for heteroaromatic carbonium ions; particularly the xanthylium derivatives are much less known and have not yet been directly characterized. The only exception is that of xanthylium ion for which Deno and his coworkers reported[3] the uv absorption spectrum in concentrated sulfuric acid.

In view of the current interest in the synthesis[4] and reactivity[5,6] of some xanthen-9-yl derivatives, we have undertaken a spectroscopic study, based on NMR, which is customarily considered one of the best sources of information in studying the structure and the charge distribution of carbocations.[7]

We report here a detailed analysis of the proton and carbon NMR spectra of the already known xanthylium ion **1** and of the highly stable ions **2** and **3**. The latter two compounds are involved as intermediates in a new recently described regiospecific reaction of substituted phenol salts[8] and are sufficiently stable to be isolated as deep red crystals.



| | X |
|---|---|
| **1**, | $CH^+$ |
| **4**, | $CH_2$ |



| | R | X |
|---|---|---|
| **2**, | H | $CH^+$ |
| **3**, | Br | $CH^+$ |
| **5**, | H | $CH_2$ |
| **6**, | Br | $CH_2$ |

While providing additional experimental evidence of their ionic structures, we suggest an interpretation of the observed chemical shifts in terms of positive charge density and ring current effect.

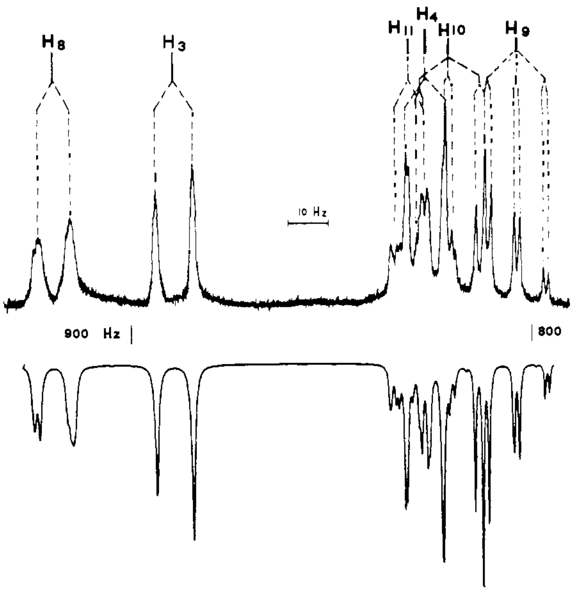


**Figure 1.** $^1$H NMR spectrum of dibenzo[*a*,*j*]xanthylium ion (**2**): experimental (top) and calculated (bottom). The broad singlet at low field is not shown.

## Experimental Section

**Materials.** Carbonium ion precursor was the carbinol for compound **1**; chloride salts of dibenzoxanthylium ion (**2**) and dibromodibenzo[*a*,*j*]xanthylium chloride (**3**) were obtained as reported[8] starting from 2-naphthyloximagnesium bromide and 6-dibromo-2-naphthyloximagnesium bromide, respectively. The corresponding neutral molecules dibenzoxanthene (**5**) and 10,10′-dibromodibenzoxanthene (**6**) were obtained by quenching the reaction mixture of the salt with saturated aqueous $NH_4Cl$ solution. NMR samples were made up to 0.5 *M* concentration by the addition of a known volume of $D_2SO_4$ (98%) for **1** and $CF_3COOD$ for **2** and **3**. The solvent for the saturated parent compounds **4**, **5**, and **6** was $Me_2SO$-$d_6$.

**Measurement of the Spectra.** Proton spectra were determined at 100 MHz on a Varian HA 100 and at 270 MHz on a Bruker spectrometer. Carbon spectra were obtained at 22.63 MHz in the FT mode on a Bruxer HFX 90. Pulse width of 3 μsec was used. Interferograms were stored in 8K memory, and dwell time ranged from 92 to 276 μsec corresponding to spectral windows from 240 to 80 ppm for partial spectra. The selective proton decoupled spectra were obtained with 0.3 W of decoupling power.

## Analysis of the Spectra

**Proton Spectra.** The assignment of the 270-MHz spectrum of **1** was obtained as follows. $H_2$ and $H_3$ were recognized because of their multiplicity (false triplet), and $H_2$ was assigned at high field considering the shielding effect of the oxygen in the para position. The remaining two protons were distinguished by irradiation of $H_2$ which produces coalescence of $H_1$ only. The coupling constants obtained from a first-order analysis (ABMX system) were checked by computer simulation of the spectrum of the four spins system $H_1$, $H_2$, $H_3$, and $H_4$ in comparison with the experimental spectrum in which any possible broadening due to small long-range coupling with $H_7$ was eliminated by irradiation of the latter signal.

The spectrum of ion **2** consisted of a broad singlet at low field, of an AB system for proton $H_3$ and $H_4$, and finally of a four spin system due to the protons $H_8$, $H_9$, $H_{10}$, and $H_{11}$ (see Figure 1). Irradiation of the low-field singlet, assigned to $H_7$ on the basis of its relative intensity, produced a considerable sharpening of the high-field part of the AB system. From this result, we could attribute the high-field absorption to $H_4$ considering the W-shaped long-range coupling $J_{H_4\text{-}H_7}$.[8] Moreover by irradiation of the low-field doublet at $\delta$ 9.20, the four spin system was reduced to a three spin system of the ABX type easily analyzed. The only ambiguity which remained at this stage was the assignment of the signal at $\delta$ 9.20 which could be either $H_8$ or $H_{11}$. This difficulty was overcome by studying the spectrum of ion **3**; it had two bromine atoms in positions 10 and 10′ and allowed the comparison of the chemical shifts of $H_8$, $H_9$, and $H_{11}$ in the molecules **2** and **3**. Namely $H_8$ was recognized on the basis of its ortho coupling and of the high-field shift from 9.20 to 9.07 in going from **2** to **3** because of the meta effect of bromine.

The interpretation of the spectrum of **3**, on which all the previous assignments rely, was straightforward because it consisted of six well-separated signals easily attributed by first-order analysis (see Figure 2). The chemicalshifts and coupling constant were checked by computer simulation of all spectra.[9] The rms between observed and calculated line

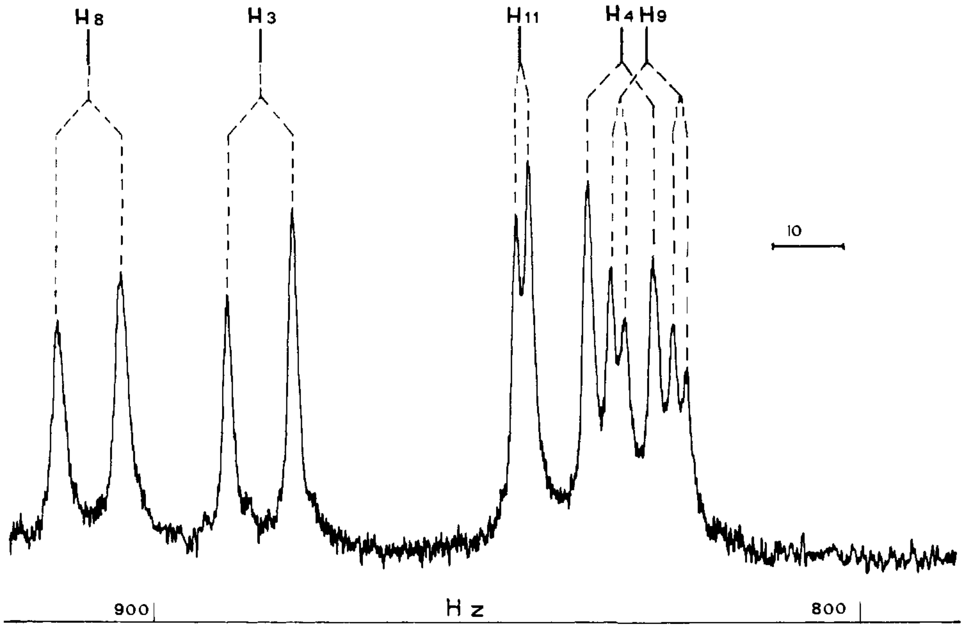


**Figure 2.** $^1$H NMR spectrum of 10,10′-dibromodibenzo[*a*,*j*]xanthylium ion (**3**).

Table I. $^1$H NMR Parameters of Xanthyl Cations

| Position[a] | 1 | 2 | 3 |
|---|---|---|---|
| 1 | 8.605 | | |
| 2 | 8.153 | | |
| 3 | 8.680 | 8.905 | 8.827 |
| 4 | 8.438 | 8.284 | 8.314 |
| 7 | 10.175 | 11.050 | 11.105 |
| 8 | | 9.208 | 9.067 |
| 9 | | 8.062 | 8.259 |
| 10 | | 8.214 | |
| 11 | | 8.310 | 8.452 |
| **Coupling constant** | **1** | **2** | **3** |
| $J_{12}$ | 7.71 | | |
| $J_{13}$ | 3.72 | | |
| $J_{23}$ | 6.05 | | |
| $J_{24}$ | 1.04 | | |
| $J_{34}$ | 9.15 | 9.14 | 9.25 |
| $J_{74}$ | 0.51 | 0.53 | 0.50 |
| $J_{89}$ | | 8.50 | 8.75 |
| $J_{8,10}$ | | 1.14 | |
| $J_{8,11}$ | | 0.39 | |
| $J_{9,10}$ | | 7.60 | |
| $J_{9,11}$ | | 0.88 | 1.7 |
| $J_{10,11}$ | | 9.22 | |

[a] All chemical shifts are in parts per million downfield from $Me_4Si$ as external standard.

positions were in each case less than 0.1 Hz. For the spectrum of compound **2** after the initial analysis of the two and four spin systems separately, the whole spectrum was calculated for a number of possible values of the long-range inter-ring and cross-ring couplings, and the final values given in Table I were chosen on the basis of the best fitting between the calculated and observed spectra. As an example of the obtained agreement, the computed spectrum of **2** is reported in Figure 1 (bottom trace).

**Carbon Spectra.** The proton noise decoupled $^{13}C$ spectrum of **1** consists of seven signals in the region of aromatic carbons (see Figure 3). Assignment of the low-field signal to the resonance of C-7 was based on its relative intensity which is one-half of that of the remaining CH's.

The single frequency off-resonance (SFOR) proton decoupled spectrum enables us to distinguish the two ring-junction carbons C-5 and C-6 since their signals are singlets; C-5 was unequivocally assigned to the lower field signal according to the $\alpha$ deshielding effect of the oxygen atom. The remaining CH signals (doublets in the SFOR spectrum) C-1, C-2, C-3, and C-4 were assigned by the single frequency selective decoupling from the corresponding protons.[10] This assignment relies on that of the proton spectrum, and each doublet was completely decoupled by irradiation respectively at $H_1$, $H_2$, $H_3$, and $H_4$ resonances.

The proton decoupled spectrum of **2** shows 11 signals, two of which have accidentally identical shift (lines 9 and 10 in Figure 4). The SFOR spectrum shows four singlets and seven doublets in agreement with the proposed structure.[4] Assignment of doublets due to the C-3, C-4, C-7, and C-8 was obtained by selective decoupling from the corresponding protons (see Figure 5), and C-7 resonance was also confirmed by its relative low intensity (see line 7 in Figure 4) as for compound **1**.

The two singlets due to C-5 and C-6 were straightforwardly assigned by comparison with the corresponding signals in the xanthylium cation. The remaining two singlets were assigned to C-1 and C-2 by observing their chemical shifts after introducing two bromine atoms in the symmetric position 10 and 10′, i.e., compound **3**.

C-1 129.6 → 128.0 (−1.6 *p*-Br effect)

C-2 132.6 → 134.1 (1.5 *m*-Br effect)

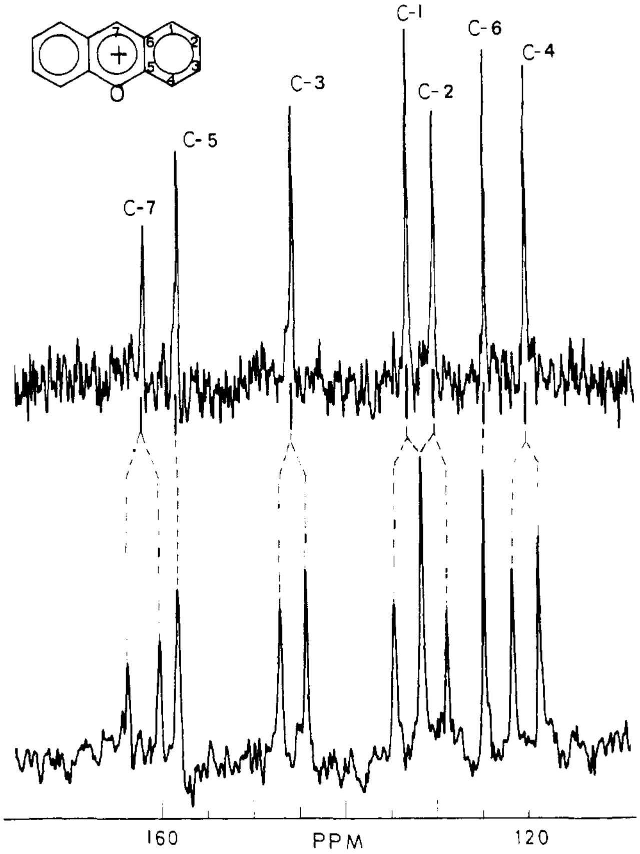


**Figure 3.** PFT-$^{13}C$ NMR spectrum of xanthylium ion (**1**): broad band decoupled (top) and off-resonance decoupled (bottom).

The same procedure was used to assign the last three CH signals:

C-10 132.2 → 126.4 (−5.8 $\alpha$-Br effect)

C-9 132.2 → 134.7 (2.5 *o*-Br effect)

C-11 133.6 → 137.0 (3.4 *o*-Br effect)

Chemical shifts for the charged and neutral compounds[11] are shown in Table II.

## Results and Discussion

All the above data can be used to get an insight into the ionic structure of compounds **1**, **2**, and **3**. A preliminary evidence of the same sp$^2$ hybridization of C-7 is given by the size of the direct coupling constant: 166.2 Hz in **1** and 165.8 Hz in **2**. However concerning the extent of charge delocalization, the observed chemical shifts values should reflect changes in the charge density.[13] In order to check this statement, the latter parameter was calculated using both the all-valence electron molecular orbital method CNDO/2[14] and EHMO[16] for the case of ions **1** and **2** (the former program does not handle four row elements) and for the corresponding neutral parent molecules (see Table III). Linear correlations of electron densities calculated by simple MO method and extended Hückel technique with proton chemical shifts have been given for neutral and charged carbocyclic aromatic species.[17] The proportionality constant $K$ is usually taken to be approximately 10 ppm per unit charge. However, the proton shifts for our compounds in strongly acidic solution do not show any linear correlation with electron densities obtained from EH method[18] as well as from CNDO calculation.

Although systematic studies of the effect of concentration were not carried out, all proton shifts were found to be

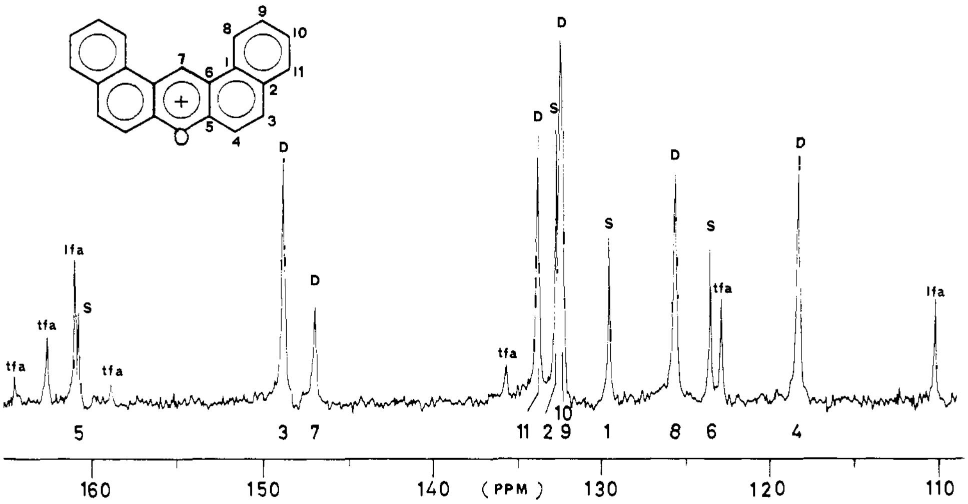


Figure 4. PFT-$^{13}C$ NMR spectrum of ion 2. Capital letters indicate SFOR multiplicity. C atoms are numbered according to the formula.

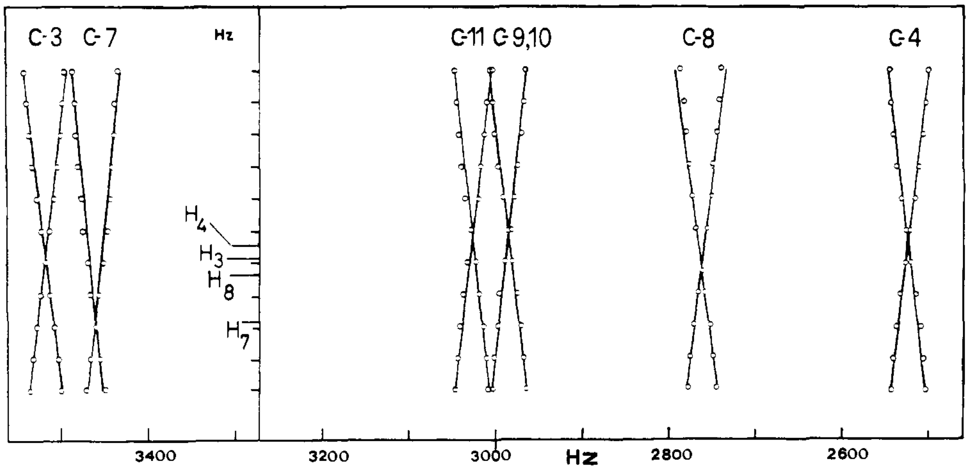


Figure 5. Correlation between carbon and proton assignments of ion 2: proton irradiation frequency (vertical axis) vs. carbon-13 observation frequency (horizontal axis).

Table II. $^{13}C$ NMR Parameters

| Carbon[a] | 1 | 4 | 2 | 5 | 3 |
|---|---|---|---|---|---|
| 1 | 132.6 | 128.9 | 129.6 | 129.0 | 128.0 |
| 2 | 129.7 | 123.0 | 132.6 | 131.8 | 134.1 |
| 3 | 145.8 | 127.7 | 148.5 | 127.9 | 147.7 |
| 4 | 119.3 | 116.6 | 118.2 | 116.2 | 119.2 |
| 5 | 159.6 | 152.1 | 160.8 | 147.5 | 161.5 |
| 6 | 124.0 | 120.8 | 123.7 | 110.2 | 124.3 |
| 7 | 162.6 | 27.91 | 146.8 | 23.4 | 146.8 |
| 8 | | | 125.4 | 123.2 | 127.4 |
| 9 | | | 132.2 | 127.2 | 134.7 |
| 10 | | | 132.2 | 126.7 | 126.4 |
| 11 | | | 133.6 | 122.6 | 137.0 |

| $^1J_{C-H}$ | 1 | 4 | 2 |
|---|---|---|---|
| $C_1$–H | 166.6 | 155.2 | |
| $C_2$–H | 168.7 | 148.5 | |
| $C_3$–H | 166.6 | 158.6 | 164.8 |
| $C_4$–H | 170.8 | 146.5 | 173.1 |
| $C_7$–H | 166.2 | 135.0 | 165.8 |
| $C_8$–H | | | 161.5 |
| $C_9$–H | | | 159.8 |
| $C_{10}$–H | | | 159.8 |
| $C_{11}$–H | | | 160.0 |

[a] Chemical shifts in parts per million referred to external $Me_4Si$, coupling constants in hertz.

Table III. Total Positive Charge Densities Calculated by CNDO/2

| Carbons | 1 | 4 | 3 | 5 |
|---|---|---|---|---|
| 1 | 0.0723 | 0.0050 | 0.0578 | 0.0256 |
| 2 | −0.0090 | −0.0030 | 0.0046 | 0.0318 |
| 3 | 0.1027 | 0.0137 | 0.0880 | 0.0024 |
| 4 | −0.0510 | −0.0239 | −0.0700 | −0.0249 |
| 5 | 0.2330 | 0.1378 | 0.2650 | 0.1474 |
| 6 | −0.0420 | −0.0053 | −0.0598 | −0.0350 |
| 7 | 0.2010 | 0.0122 | 0.1418 | 0.0116 |
| 8 | | | −0.0213 | −0.0175 |
| 9 | | | 0.0465 | 0.0109 |
| 10 | | | 0.0040 | 0.0021 |
| 11 | | | 0.0319 | −0.0001 |

dependent on concentration. The H-7 proton resonance changed by up to 1 ppm as the concentration increased. Concerning the latter result, it must be pointed out that association affects such ion pairs or higher aggregates,[19] and aromatic ring current effects can play an important role in determining the observed chemical shifts. This observation suggests that proton chemical shift is not the proper parameter for the evaluation of charge density in aromatic cations of the type examined in the present work.

A better result has been obtained in the correlation between experimental $^{13}C$ shifts and calculated ground state total electron density $\rho_t$ which is shown in Figure 6. The line of the best fit is represented by the equation:

$$\delta = (151.9 \pm 9.08)\rho_t + 126.3 \qquad (1)$$

with a least-squares correlation coefficient of 0.95. This correlation, while good with CNDO method (low standard error of the coefficient), did not afford any linear relation with similar calculation based on EHMO.

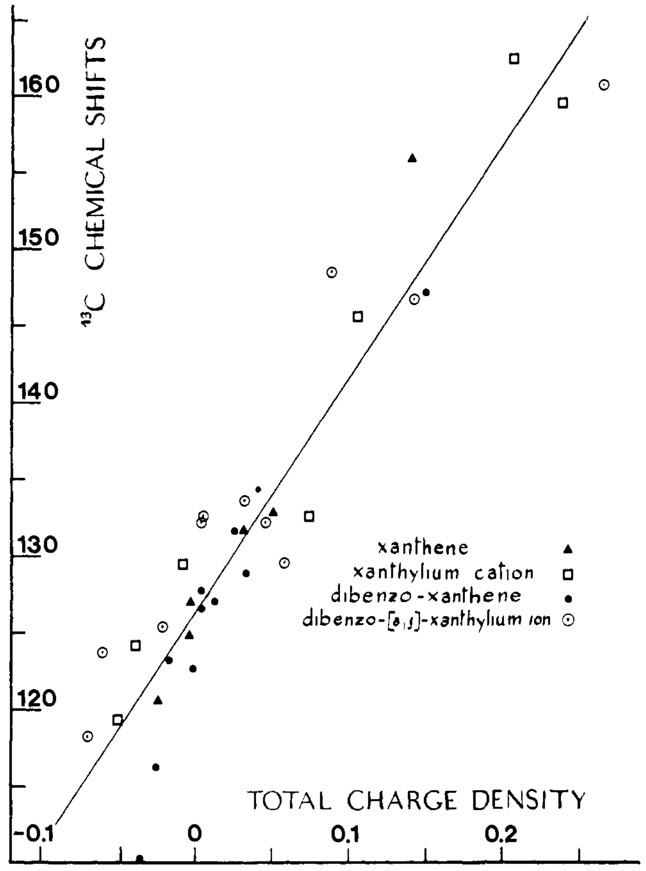


**Figure 6.** Plot of experimental aromatic $^{13}$C chemical shifts vs. total charge density (CNDO) of neutral (**4** and **5**) and charged (**1** and **2**) species. The least-square correlation line is indicated.

Correlations based on CNDO/2 charge densities have been previously reported for a number of aromatic compounds.[18a,20] The results of the present work provide a reliable experimental measure of the excess of positive charge at least in this closely related series of neutral and charged molecules by using the eq 1 and without performing CNDO calculations.

It is further proved that, in the case of xanthylium ion derivatives, the positive charge is extremely delocalized in agreement with MO calculations. This situation is considerably different from that previously observed in other nonheteroaromatic cations such as diphenyl and triphenyl carbonium ions where the carbenium center carries a relatively large fraction of the positive charge as shown by their shift values of 202.2 and 212.7 ppm, respectively.[2] Thus the degree of delocalization found for xanthylium ion derivatives is in keeping with their planarity and with their high stability.

The $^{13}$C NMR resonance is a useful technique for determination of heteroaromatic cation structures. While the correlation of $^1$H chemical shifts with charge density is not observed because of the large influence of additional shielding effects, the $^{13}$C shifts are in agreement with the positive charge distribution of the alternant heterocyclic aromatic structures derived from simple resonance considerations in that the positive charge is delocalized from C-7 onto the C-1, C-3, C-5, C-9, and C-11 positions.

**Acknowledgments.** The authors are greatly indebted to Professor G. Casnati and Dr. G. Casiraghi for samples **2** and **3**.

## References and Notes

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(20) (a) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94**, 3089 (1972); (b) R. G. Jones and P. Partington, *J. Chem. Soc.*, 2087 (1972); (c) R. J. Pugmuire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 4232 (1968); **90**, 697 (1968).