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APPLICATION OF NUCLEAR QUADRUPOLE RESONANCE TO ORGANIC CHEMISTRY

PROBING DELOCALIZATION EFFECTS IN TETRACHLOPENTAFULVENES[1]†

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Abstract—The ^{35}Cl quadrupole resonance frequencies of a series of 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes (**2**, R_1 = H, R_2 = Aryl) and related substances were determined at 77°K. The results indicate the negligible contribution of the delocalized 'aromatic' cyclopentadienide structures in the ground-state. In the relatively dipolar *p*-dimethylaminophenyl and triapentafulvalene derivatives (**9** and **11**, respectively), the partial negative-charge is not distributed evenly in the five-membered ring but is localized mostly in the vicinity of the fulvenic double bonds. In most of the 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes under study, the NQR absorptions of the chlorine nuclei Z to the aryl groups are considerably shifted to higher frequencies. The effect, which is most pronounced in the 6,6-diphenyl derivative (**10**), is explained in terms of the spatial structures of the compounds and their substantial deviations from planarity.

Pure nuclear quadrupole resonance (NQR) studies in molecular crystals have been applied to the determination of the distribution of molecular electrons.[2-7] During the past decade, NQR spectroscopy has emerged as a structural tool in organic chemistry (including organometallic chemistry), particularly in the family of chlorocarbons.[8-14] It has been shown that the variation in the ionic character is the dominant effect by which an external electric field modifies the NQR frequencies of a chlorine atom bonded to a C atom.[6,15] According to the theory of Townes and Dailey,[6,16] an increase in the ionic character should be accompanied by a decrease in the NQR frequency of the Cl atom. Conversely, a drop in the ionicity should elevate the chlorine molecular quadrupole coupling constant. Following these fundamental guidelines, we have applied NQR spectroscopy as a probe for evaluating the "aromatic" character in Cl-substituted pentafulvenes.

The fulvenes have attracted the interest of the chemist since the turn of the century.[17-21] The pentafulvenes are cross-conjugated non-alternant, non-benzenoid systems which "occupy a position intermediate between their benzenoid isomers and the olefins"[22] in respect to their bonding and reactivity. Pentafulvenes have frequently been represented as resonance hybrides of the localized Kekulé structure **1** and the "aromatic" dipolar structure **1a**. The problem of 'aromaticity' in the pentafulvenes is associated with the relative contribution, in the ground-state, of the aromatic structure **1a** in which the system formally achieves a Hückel 6π electron configuration by delocalization of the π electrons in the exocyclic C=C into the 5-membered ring. The partial charge in the 5-membered ring may be estimated experimentally, for example, from ^{13}C NMR data[23] and from dipole moment data. Dipole moments have frequently served as a probe for evaluating the degree of delocalization in non-alternant non-benzenoid aromatic compounds.[24] The dipole moment of the parent compound pentafulvene, as determined by microwave spectroscopy is only 0.49D,[25] indicating the absence of any significant contribution of an "aromatic" structure **1a** in the 5-membered ring. Lack of aromatic character was also the result of an electron diffraction study of 6,6-dimethylpentafulvene.[26]

In order to increase the relative contribution of **1a** type structure to the ground-state resonance hybride, substituents were introduced at the exocyclic C atom C(6) which are able to stabilize the positive charge on C(6). An example is 6,6 - bis(N,N - dimethylamino)pentafulvene[27] with a dipole moment of 5.4D, indicating the delocalization of the partial positive charge into the N atoms. Alternatively, the picture of bond alternation may perhaps be altered by the introduction of electron withdrawing substituents at the 5-membered ring which are able to stabilize the negative charge developed in the ring. The 1,2,3,4 - tetrachloropentafulvenes (**2**) illustrate such an attempt. The four Cl atoms at the 5-membered ring of **2**, by virtue of their inductive electron withdrawing power, could perhaps contribute towards an effective π-electron delocalization in the ring. The dipole moment of 1,2,3,4 - tetrachloro - 1,3 - cyclopentadiene (**3**) (in benzene solution) is 1.55D,[28] while the corresponding moment of 1,2,3,4 - tetrachloro - 6 - phenylpentafulvene (**4**) is 2.86D.[29] Does the dipole moment of **4** express a significant contribution of the dipolar 'aromatic' structure **4a** in the ground-state? It has been suggested that the existence of large dipole moments cannot in itself be taken as evidence that a molecule has a highly delocalized aromatic character.[30] The dipole moment is a global, overall

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property of the molecule; its breakdown to contributions of the different parts of the molecule is not necessarily unequivocal. Sometimes, it does not permit to pinpoint the π-electron delocalization in particular regions of the molecule. Thus, in the case of **4**, it may be argued that the dipole moment is primarily due to contributions of dipolar structures in which the negative charge is not delocalized in the 5-membered ring, but localized in the vicinity of the exocyclic C=C, e.g. **4b**, **4c**. In an endeavour to shed light upon the local distribution of the electrons in 1,2,3,4 - tetrachloropentafulvenes (**2**) and the extent of the delocalization of the partial negative charge in their 5-membered rings, we investigated the ^{35}Cl quadrupole resonance spectra of a series of 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes (**4–9**), and related substances.

The ^{35}Cl quadrupole resonance frequencies of six 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes (**4–9**), 1,2,3,4 - tetrachloro - 6,6 - diphenylpentafulvene (**10**), 1,2,3,4 - tetrachloro - 5,6 - diphenyltriapentafulvalene (**11**) hexachloropentafulvene (**12**), octachloropentafulvalene (**13**) and $n\text{-Bu}_4\text{P}^+\text{C}_5\text{Cl}_5^-$ (**14**) are given in Table 1. The validity of the NQR method depends on correct assignments of the wealth of resonances (obtained experimentally) to the different Cl atoms present in the molecule under study. However, such a task may become difficult when the separation between the various frequencies is small. Under such circumstances, the possibility that the frequency separation is solely due to non-specific *inter*molecular forces should be borne in mind.[7,8,31] The following analysis of the data permits only a partial assignment of the frequencies in each spectrum. It is sufficient, however, to form a solid basis for providing qualitative answers to the questions posed at the outset (*vide supra*).

The spectrum of each tetrachloropentafulvene under study contained four lines (absorptions) in equal intensity. Each line was attributed to one of the four Cl atoms in the molecule. The normal region of NQR frequencies of the tetrachloropentafulvene system was estimated from the ^{35}Cl quadrupole resonance spectrum of **3**. It consists of two frequencies at 36.128 and 36.298 MHz, the average of which, viz. 36.213 MHz was taken as a reference (ν_0). Table 1 contains also the difference ($\nu_{max} - \nu_{min}$) between the extreme frequences (ν_{min}, ν_{max}) and their shifts from the reference frequency ($\nu_0 - \nu_{min}$ and $\nu_{max} - \nu_0$).

In the spectra of all the 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes under investigation (**4–8**), except the *p* - dimethylaminophenyl derivative (**9**), the shifts of the maximum from the reference frequency ($\nu_{max} - \nu_0$) are substantial, while the corresponding shifts of the minimum from the reference frequency ($\nu_0 - \nu_{min}$) are negligible. In each of these spectra, one frequency is outstanding as compared with the other three frequencies, which are much closer to ν_0. Among the four Cl nuclei in each 6 - aryl - 1,2,3,4 - tetrachloropentafulvene, one chlorine, Cl-4, is unique in being on the same side ("zusammen") of the aryl group. It is therefore reasonable to assign ν_{max} to Cl-4. This assignment is strikingly verified by the NQR spectrum of the symmetrical 6,6 - diphenyl - 1,2,3,4 - tetrachloropentafulvene (**10**) which contains *two* lines at higher frequencies representing Cl-1 and Cl-4 and one line of double intensity at normal frequencies representing Cl-2 and Cl-3. (At ambient temperature, four lines are observed.) Once the assignments of Cl-4 in compounds **4–8** are established, the remainder of the spectrum should be attributed to Cl-1, Cl-2, and Cl-3. The evidence shows that the lines representing these chlorines are hardly shifted to lower frequencies relative to ν_0. In most cases, only one line in each spectrum is slightly shifted in this direction, while the remaining two lines are shifted somewhat to higher frequencies. In any event, these results indicate that in the 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes, as well as in **10**, the Cl atoms farther away from the exocyclic double bond (Cl-2 and Cl-3) absorb at normal frequencies. This conclusion holds true even in such extreme cases as the *p*-nitrophenyl and the *p*-anisyl derivatives (**5** and **8**, respectively) with dipole moments in opposite direction. The excess negative charge in the 5-membered ring would have been repelled by the lone pairs of the chlorines, giving more ionic C–Cl bonds and hence lower NQR frequencies.[32] Indeed, such an effect has been observed in a series of pentachlorocyclopentadienide salts (e.g., **14**).[32,33] The absence of such NQR frequencies in the spectra of **4–8** and **10** means that the partial negative charge is barely, if at all, delocalized in the 5-membered ring of the tetrachloropentafulvenes. The contribution of the "aromatic" cyclopentadienide structures (of the **4a** type) in the ground-state is therefore negligible.

The NQR spectrum of the *p*-dimethylaminophenyl

Table 1. The ^{35}Cl quadrupole resonance frequencies (ν) of 6-aryl-1,2,3,4-tetrachlorpentafulvenes and related compounds at 77°K (in MHz)

Compound	ν				$\nu_{max} - \nu_{min}$	$\nu_0 - \nu_{min}$	$\nu_{max} - \nu_0$	μ[b]
3	36.128	36.298			0.170	0.085	0.085	1.55[28]
4	36.182	36.390	36.411	36.904	0.722	0.03	0.69	2.86[c]
5	36.168	36.541	36.674	37.167	0.999	0.04	0.95	
6[a]	36.174	36.634	36.719	36.930	0.756	0.04	0.71	1.78[c]
7	35.996	36.329	36.690	36.806	0.810	0.22	0.59	1.63[c]
8	36.114	36.194	36.273	36.943	0.829	0.10	0.73	4.16[d]
9	35.777	35.795	36.104	36.575	0.798	0.44	0.36	6.82[d]
10	36.250	36.250	37.150	37.625	1.375	-0.04	1.42	
11	35.422	35.480	35.822	36.452	1.030	0.79	0.24	8.1[29]
12[38]	36.783	37.163	37.805	38.086	1.520	-0.57	2.09	1.00[c]
	38.179	38.303						
13[39]	36.570	36.584	37.673	37.786	1.216	-0.36	1.58	0.40[c]
14[33]	35.20	35.28	35.33	35.50	0.48	1.01	-0.53	
	35.68							

a) The para chlorine atom absorbs at 34.676 MHz.

b) Dipole moment values, in Debye units, at 30°C, in cyclohexane solution. The values of **9** and **11** are in benzene solution.

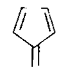
c) I. Agranat, H. Weiler-Feilchenfeld, and R. M. J. Loewenstein, Chem. Comm., 1153 (1970).

d) R. M. J. Loewenstein, M Sc. Thesis, The Hebrew University of Jerusalem, Jerusalem, 1968.

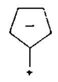
derivative (**9**) is exceptional: the value of $\nu_0-\nu_{min}$, 0.44 Hz, is substantial. Furthermore, the spectrum of **9** contains two lines, at 35.777 and 35.795 MHz which are significantly shifted to lower frequencies relative to ν_0. The assignments made above in the 6 - aryl - 1,2,3,4 - tetrachloropentafulvene series should be reversed in the case of **9** as follows. The two downfield lines must be assigned to Cl-1 and Cl-4. The remaining two lines, at 36.104 and 36.575 MHz should therefore be attributed to Cl-2 and Cl-3. In spite of the "reverse assignment" of Cl-1 and Cl-4, the Cl atoms farther away from the fulvenic double bond (Cl-2 and Cl-3) absorb at normal frequencies. One is forced to conclude that even in **9** which has a considerable dipole moment of 6.82D towards the 5-membered ring, the partial negative charge is not delocalized in the C_5 ring and the contribution of the "aromatic" structure **9a** in the ground state is not significant.[34] On the other hand, in **9**, a certain contribution of a dipolar structure in which the negative charge is localized in the vicinity of the fulvenic bond, e.g. **9c**, is called for. Such a contribution may account for the shift to lower NQR frequencies of Cl-1 and Cl-4, and for the high value of the dipole moment.

The substantial elevation of the NQR frequency of Cl-4 in all the 6 - aryl - 1,2,3,4 - tetrachloropentafulvenes (except **9**) and of the frequencies of Cl-1 and Cl-4 of **10** should be noted. The effect is hardly sensitive to the *para* substituent on the phenyl ring. $\nu(\text{Cl-4})-\nu_0 = 0.95$, 0.69 and 0.71 MHz for **5**, **4** and **8**, respectively. It is probably caused by a Stark-effect repulsion of p_y lone pairs on chlorine by filled π-electrons of the phenyl rings. One may conclude, on the basis of the NQR spectra, that for steric reasons, the 6 - aryltetrachloropentafulvenes are not planar and that the phenyl rings in these systems do not lie in the plane of the 5-membered ring. The bond connecting the phenyl ring and the exocyclic C atom (C-6) is considerably twisted and Cl-4 is probably situated, to a certain degree, above the plane of the aromatic ring. In the case of **10**, the shifts to higher NQR frequencies of the Cl nuclei Z to the aryl groups (Cl-1 and Cl-4) are striking: $\nu(\text{Cl-4})-\nu_0 = 1.42$ MHz; $\nu(\text{Cl-1})-\nu_0 = 0.94$ MHz; $(\nu(\text{Cl-4, Cl-1})-\nu_0)_{average} = 1.18$ MHz. The steric demands of the two *gem*-phenyl groups lead to a greater deviation from planarity (Aryl versus C_5Cl_4 ring) and twist of the Aryl–C-6 bond than in the monoaryl derivatives (**4**–**8**). The effect illustrates the potential inherent in the NQR method of obtaining qualitative information pertaining to the spatial structures of overcrowded organic molecules. In **9**, the effect of the dipolar structures on the NQR frequency of Cl-4 (and Cl-1) overwhelms the opposing effect of the aryl group.

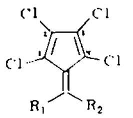
The NQR spectrum of the triapentafulvalene **11** is particularly interesting. It is completely different from that of compounds **4**–**8** and **10**, but qualitatively it resembles the spectrum of **9**. $\nu_{max}-\nu_0$ is only 0.24 MHz while $\nu_0-\nu_{min}$ is 0.79 MHz. Thus, ν_{max} (36.452 MHz) represents Cl-2 (or Cl-3) while ν_{min} (35.422) represents Cl-1 (or Cl-4). In spite of the high dipole moment (8.1D,[29] 7.97D[35]), the line representing Cl-2 appears at ordinary frequencies. The shift of the lines representing Cl-1 and Cl-4 to much lower frequencies may be attributed to the effect of the 3-membered ring and its partial positive charge. In the 5-membered ring, the partial negative charge is not distributed evenly but is localized mostly in the vicinity of the "pinch", indicating a considerable bond alternation in the 5-membered ring and the absence of "cyclopropenium - cyclopentadienide aromaticity" (structure **11a**) in the ground-state. This picture may be reflected in a certain contribution of a dipolar structure of the type **11c** which may also account for the dipole moment of the molecule. These findings are in accord with the bond lengths observed in the X-rays crystallographic studies of



1



1a



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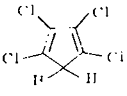

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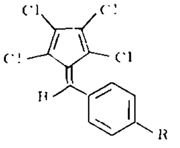


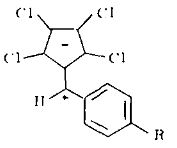
4, R = H

5, R NO_2

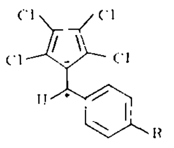
6, R - Cl

7, R - F

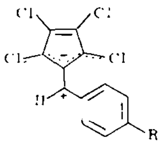
8, R - OMe



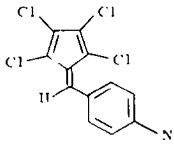
4a, R - H



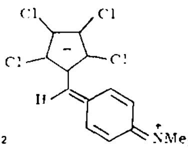
4b, R - H



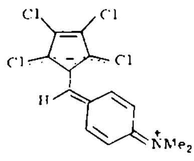
4c, R - H



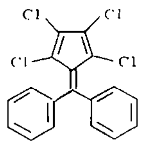
9



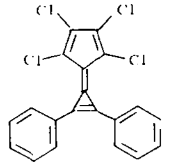
9a,



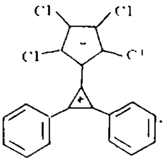
9c



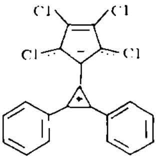
10



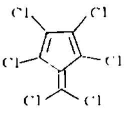
11



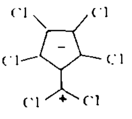
11a



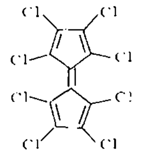
11c



12



12a



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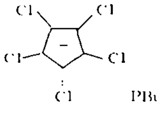

14

11[36] (and of its 5,6-dipropyl analog[37]). The results indicated a (small) deviation from a complete bond alternation only in the triafulvene moiety of the molecules, while the 5-membered rings proved to possess a truly classical polyolefinic character.

Finally, the NQR spectra of the perchlorocarbon compounds 12[13,38] and 13[39] should be mentioned. As previously shown,[38] in perchloropentafulvene (**12**), Cl-2 and Cl-3 are represented by two lines at the 37.0 MHz region, while Cl-1, Cl-4, Cl-6 and Cl-6′ are represented by four lines at the 38.1 MHz region. The NQR spectrum of **12** does not indicate the presence of a contribution of the dipolar aromatic structure (**12a**) to the ground-state of **12**. The shift to higher frequencies of the Cl nuclei ortho to the fulvenic double bond was explained in terms of the strong perturbations of the electrons of Cl-1 and in the C-1–Cl-1 bond produced by the C-6–Cl-6 dipole. In **13**, the "distant" Cl nuclei (Cl-2, Cl-3, Cl-6 and Cl-7) are represented by two lines centered at the 36.6 MHz region, while Cl-1, Cl-4, Cl-5 and Cl-8 are represented by two lines centered at the 37.7 MHz region. The shift to higher frequencies of the four chlorine nuclei ortho to the pinch of **13** was interpreted as due to non-covalent intramolecular interactions of the bucking C–Cl groups.[39] The normal position of the four "distant" Cl nuclei should be noted. In any event, the NQR spectra of the two perchlorocarbon compounds reveal (somewhat) their unique spatial structures, but do not point towards any fulvenic characteristics.

EXPERIMENTAL

Most of the NQR measurements were carried out at 77°K using a regenerative detector[40] and were observed on the oscilloscope screen with a signal-to-noise ratio of 10:1. Frequencies were determined within ±0.001 MHz. The NQR spectrum of **10** was recorded on a Decca Radar NQR Spectrometer, using Zeeman modulation. Decca frequencies are estimated to be accurate to 0.007 MHz.

M.ps were taken on a Unimelt Thomas and Hoover capillary mp apparatus and were uncorrected. Most of the compounds studied were prepared according to literature procedures.

1,2,3,4 - *Tetrachloro* - 1,3 - *cyclopentadiene* (**3**). Reduction of hexachlorocyclopentadiene with Zn and AcOH, according to Roeding and Horning[41] gave **3**, as colourless crystals, m.p. 62° (from MeOH); lit.[41] m.p. 63.5–64°).

The 6 - aryl - 1,2,3,4, - tetrachloropentafulvenes were prepared according to the method of McBee *et al.*,[42] by condensation of **3** and the appropriate aldehyde in boiling abs EtOH.

1,2,3,4 - *Tetrachloro* - 6 - *phenylpentafulvene* (**4**) was obtained as red needles, m.p. 81° (from hexane); (lit.[42] m.p. 81–82°).

1,2,3,4 - *Tetrachloro* - 6 - (p - *nitrophenyl*)*pentafulvene* (**5**) was obtained as brown-purple needles, m.p. 197° (from 1-BuOH); (lit.[43] m.p. 196.5–197°).

1,2,3,4 - *Tetrachloro* - 6 - (p - *chlorophenyl*)*pentafulvene* (**6**) was obtained as red needles, m.p. 142° (from MeOH); (lit.[42] m.p. 142–143°).

1,2,3,4 - *Tetrachloro* - 6 - (p - *fluorophenyl*)*pentafulvene* (**7**) was obtained as brown-red needles, m.p. 113.5–115° (from MeOH) in 32% yield. (Found: C, 46.44; H, 1.46; Cl, 46.19; F, 5.95. $C_{12}H_5Cl_4F$ requires: C, 46.29, H, 1.62; Cl, 45.74; F, 6.13%).

1,2,3,4 - *Tetrachloro* - 6 (p - *methoxyphenyl*)*pentafulvene* (**8**) was obtained as red needles, m.p. 125–126° (from MeOH); (lit.[42] m.p. 127–128°).

1,2,3,4 - *Tetrachloro* - 6 - (p - *dimethylaminophenyl*)*pentafulvene* (**9**) was prepared by condensation of **3** with *p* - dimethylaminobenzaldehyde in MeOH at room temp. and was obtained as red needles, m.p. 123–125° (from hexane); (lit.[42] m.p. 126–127°), yield, 52%.

1,2,3,4 - *Tetrachloro* - 6,6 - *diphenylpentafulvene* (**10**) was prepared by chlorination of 6,6 - diphenylpentafulvene according to Hafner and Schmidt.[44] N - Chlorosuccinimide (18.2 g, 136 mmole) was added, in small portions, under anhydrous conditions, to a magnetically stirred soln of 6,6 - diphenylpentafulvene (6.90 g, 30 mmole) in dry diglyme (60 ml) at 110°. After the addition was complete (10 min), the soln was stirred at 110–115° for additional 60 min. The resulting deep dark red soln was slowly poured into cold (ice) water (500 ml) and the resuting mixture was left overnight at room tem. The red solid was filtered off, washed thoroughly with water, dried, recrystallized from 2-PrOH and washed with MeOH to give **10** as a brown-red needles, m.p. 168–169°; (lit.[44] m.p. 165–168°), yield, 36%. An analytical sample was obtained by a second recrystallization from 2-PrOH. (Found: C, 58.55; H, 2.65; Cl, 38.50. $C_{18}H_{10}Cl_4$ Required: C, 58.7; H, 2.7; Cl, 38.6%).

1,2,3,4 - *Tetrachloro* - 5,6 - *diphenyltriapentafulvalene* (**11**) was prepared by a direct condensation of **3** and diphenylcyclopropenone in MeOH at room temp.[29] It was obtained as yellow needles, m.p. 197° dec (from methylcyclohexane); (lit.[29] m.p. 197° dec).

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REFERENCES

[1] Part 91 in the series: Fulvenes and thermochromic ethylenes. For Part 90; see H. L. Ammon, C. Sherrer and I. Agranat, to be published.

[2] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance*

Spectroscopy, Suppl. **1**, In *Solid State Physics, Advances in Research and Applications* (Edited by F. Seitz and D. Turnbull), p. 119. Academic Press, New York (1958).

[3] H. O. Hooper and P. J. Bray, *J. Chem. Phys.* **33**, 334 (1960).

[4] E. Scrocco in *Adv. Chem. Phys.* (Edited by I. Prigogine), Vol. V, p. 319. Interscience, New York (1963).

[5] G. Semin and E. I. Fedin, *The Mössbauer Effect and Its Applications in Chemistry* (Edited by V. I. Gol'danskii), pp. 68–119. Consultants Bureau, New York (1964).

[6] E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York (1969).

[7] K. G. Semin, T. A. Babushkina and G. G. Yakobson, *Nuclear Quadrupole Resonance in Chemistry*. Habsted-Wiley, Chichester (1975).

[8] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc.* (A) 153 (1968).

[9] A. Roedig, R. Helm, R. West and R. M. Smith, *Tetrahedron Letters* 2137 (1969).

[10] R. M. Smith and R. West, *Ibid.* 2141 (1969).

[11] D. B. Roll and F. J. Biros, *Analyt. Chem.* **41**, 407 (1969).

[12] R. M. Smith and R. West, *J. Org. Chem.* **35**, 2681 (1970).

[13] M. Hashimoto and K. Mano, *Bull. Chem. Soc. Japan* **45**, 706 (1972).

[14a] G. Wulsberg, R. West and V. N. Mallikarjuna Rao, *J. Organometal. Chem.* **86**, 303 (1975); [b] G. Wulsberg, *Ibid.* **86**, 321 (1975).

[15] R. W. Dixon and N. Bloembergen, *J. Chem. Phys.* **41**, 1720, 1739 (1964).

[16] C. H. Townes and B. P. Dailey, *Ibid.* **20**, 35 (1952).

[17] J. Thiele, *Ber. Deutsch. Chem. Ges.* **33**, 666 (1900).

[18] J. H. Day, *Chem. Rev.* **53**, 167 (1953).

[19] E. D. Bergmann, *Prog. Org. Chem.* **3**, 81 (1955).

[20] E. D. Bergmann, *Chem. Rev.* **68**, 41 (1968).

[21] P. Yates, In *Advances in Alicyclic Chemistry* (Edited by H. Hart and J. Karabatsos), Vol. 2, p. 59. Academic Press, New York (1968).

[22] K. Hafner, K. H. Hafner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem.* Internat. Edit. **2**, 123 (1963).

[23] R. Hollenstein, A. Mooser, M. Neuenschwander and W. von Philipsborn, *Ibid.* Internat. Edit. **13**, 551 (1974).

[24] I. Agranat, *Aromatic Compounds, MTP Internat. Rev. Sc.* (Edited by H. Zollinger) Organic Chemistry, Series One, Vol. 3, p. 139. Butterworths, London (1973).

[25] R. D. Brown, F. R. Burden and J. E. Kent, *J. Chem. Phys.* **49**, 5542 (1968).

[26] J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.* **92**, 261 (1970).

[27] K. Hafner, G. Schulz and K. Wagner, *Ann.* **678**, 39 (1964).

[28] Y. Kitahara, I. Murata and S. Katagiri, *Angew. Chem.* Internat. Edit. **4**, 353 (1965).

[29] E. D. Bergmann and I. Agranat, *Tetrahedron* **22**, 1275 (1966).

[30] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, pp. 181–182. McGraw-Hill, New York (1969).

[31] E. A. C. Lucken, *Tetrahedron* Suppl. 2, **19**, 123 (1963).

[32] G. Wulsberg and R. West, *J. Am. Chem. Soc.* **93**, 4085 (1971).

[33] G. Wulsberg and R. West, *Ibid.* **94**, 6069 (1972).

[34] Cf. J. Griffiths and M. Lockwood, *J. Chem. Soc.* Perkin I, 48 (1976).

[35] I. Murata, M. Ueno, Y. Kitahara and H. Watanabe, *Tetrahedron Letters* 1831 (1966).

[36] O. Kennard, K. A. Kerr, D. G. Watson and J. K. Fawcett, *Proc. Roy. Soc.* **A316**, 551 (1970).

[37] H. Shimanouchi, Y. Sasada, T. Ashida, M. Kakudo, I. Murata and Y. Kitahara, *Acta Crystallog.* **B25**, 1890 (1969).

[38] I. Agranat, M. Hayek and D. Gill, *Bull. Chem. Soc. Japan* **46**, 1575 (1973).

[39] I. Agranat, D. Gill, M. Hayek and R. M. J. Loewenstein, *J. Chem. Phys.* **51**, 2756 (1969).

[40] D. Gill, M. Hayek, Y. Alon and A. Simievic, *Rev. Sci. Instr.* **38**, 1588 (1967).

[41] A. Roedig and L. Hoerning, *Chem. Ber.* **88**, 2003 (1955).

[42] E. T. McBee, R. K. Meyers and C. F. Baranauckas, *J. Am. Chem. Soc.* **77**, 86 (1955).

[43] J. S. Meek and P. Argabright, *J. Org. Chem.* **22**, 1708 (1957).

[44] K. Hafner and F. Schmidt, *Tetrahedron Letters* 5101 (1973).