of hand to be incorrect, and the x coordinate was inverted. Hydrogen atoms were not included. Maximum and minimum peaks of 1.50 and −2.76 e Å^{-3} were found on a final difference Fourier map. The majority of these features were in the vicinity of the iodine atoms. See the paragraph at the end of the paper about supplementary material.

Registry No. 1, 82200-91-7; 2, 85939-86-2; 2 picrate, 85939-87-3; 3, 85939-88-4; 3 picrate, 85939-89-5; 4·I$^-$, 85939-90-8; 4·I$_3^-$, 85939-92-0; NaBH$_3$CN, 25895-60-7; I$_2$, 7553-56-2; 9-aza-1-thioniabicyclo[3.3.1]nonane iodide, 85956-52-1; methylamine, 74-89-5; 5-thiacyclooctanone, 20701-80-8; dimethylamine hydrochloride, 506-59-2.

Supplementary Material Available: Tables of final atomic positional parameters, anisotropic thermal parameters, and bond distances and angles (2 pages). Ordering information is given on any current masthead page.

Proton and Carbon-13 Nuclear Magnetic Resonance Spectra of Methylenecyclopropane and Proton Nuclear Magnetic Resonance Spectra of Some Methyl-Substituted Methylenecyclopropanes. A Reinvestigation

Wolfgang von der Saal,* Wolfgang Risler, Josef Stawitz, and Helmut Quast*

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, West Germany

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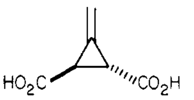
The proton nuclear magnetic resonance spectra of some methyl-substituted methylenecyclopropanes and the parent compound have been reinvestigated at high resolution and 400-MHz spectrometer frequency. That of methylenecyclopropane has been analyzed with the help of the carbon-13 satellites and the proton-coupled carbon-13 spectrum. Pseudo-INDOR experiments uncovered an unexpected positive sign of the geminal coupling constants of the vinyl protons. The spectral parameters of all compounds, optimized via LAOCOON III and LAME analysis, and the deceptively simple appearance of the AA′A″A‴XX′ spectrum of both methylenecyclopropane and the isomeric cyclobutene are discussed.

One of the early applications of proton NMR spectroscopy to organic chemistry was the solution of the long-standing structural problem of Feist's acid (1,[1,2] Chart I), the first known derivative of methylenecyclopropane. During the last decades, numerous methylenecyclopropanes have been reported, including natural products, e.g., the amino acid hypoglycin A (2)[3] and the parent compound 3.[4,5] The latter has been thorougly investigated by microwave,[6] infrared,[7] carbon-13 NMR,[8] and proton NMR spectroscopy in nematic phases.[9] Although the proton NMR spectrum has been reported for the parent compound 3,[5] a rigorous analysis of the spectra of simple alkyl-substituted methylenecyclopropanes is still lacking despite several papers devoted to the spectra of such compounds.[10-12] Only the allylic coupling constants for 6, obtained by means of a more rigorous treatment, have been reported.[13] In fact, most of the earlier spectra of alkyl-substituted methylenecyclopropanes have been determined at relatively low field and apparently sometimes with insufficient resolution. This resulted in an oversimplified (first order) interpretation which neglected small long-range couplings and therefore constituted an inadequate assignment of the spin system under investigation. For example, two different interpretations have been reported for the proton spectrum of 6,[10,12] neither one being fully acceptable. In contrast, the proton spectra of several methylenecyclopropanes with two or three substituents

Chart I



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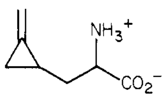

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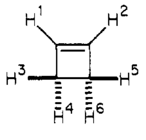

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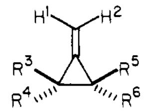

	R^4	R^5	R^6	Table
3	H	H	H	VI
4	H	H	CH$_3$	I
cis-**5**	CH$_3$	H	CH$_3$	II
trans-**5**	CH$_3$	CH$_3$	H	III
6	H	CH$_3$	CH$_3$	IV
7	CH$_3$	CH$_3$	CH$_3$	V

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Table I. LAME-Optimized Chemical Shifts (ppm; Principal Diagonal Elements) and Proton–Proton Coupling Constants (Hz; Other Elements, ^3J in Parentheses, ^4J in Brackets, ^5J in Braces) of 2-Methylmethylenecyclopropane (4) for [$^2H_6$]Benzene Solution (Figure 1)

	H^1	H^2	H^3	H^4	H^5	$H^6(CH_3)$
H^1	5.460	1.19	[−1.79]	[−1.80]	[−2.31]	{0.40}
H^2		5.512	[−2.51]	[−2.53]	[−1.66]	{0.10}
H^3			1.225	−8.52	(9.11)	[−0.13]
H^4				0.685	(5.17)	[−0.33]
H^5					1.368	(6.15)
$H^6(CH_3)$						1.137

Table II. LAME-Optimized Chemical Shifts (ppm; Principal Diagonal Elements) and Proton–Proton Coupling Constants (Hz; Other Elements, ^3J in Parentheses, ^4J in Brackets, ^5J in Braces) of *cis*-2,3-Dimethylmethylenecyclopropane (*cis*-5) for [$^2H_6$]Benzene Solution

	H^1	H^2	H^3	H^5	$H^4(CH_3)$	$H^6(CH_3)$
H^1	5.416	1.23	[−1.88]	[−2.31]	{0.14}	{0.39}
H^2		5.416	[−2.31]	[−1.88]	{0.39}	{0.14}
H^3			1.487	(10.11)	(6.46)	[−0.25]
H^5				1.487	[−0.25]	(6.46)
$H^4(CH_3)$					1.091	{0}
$H^6(CH_3)$						1.091

Table III. LAME-Optimized Chemical Shifts (ppm; Principal Diagonal Elements) and Proton–Proton Coupling Constants (Hz; Other Elements, ^3J in Parentheses, ^4J in Brackets, ^5J in Braces) of *trans*-2,3-Dimethylmethylenecyclopropane (*trans*-5) for [$^2H_6$]Benzene Solution

	H^1	H^2	H^3	H^6	$H^4(CH_3)$	$H^5(CH_3)$
H^1	5.511	1.25	[−1.75]	[−2.25]	{0.10}	{0.35}
H^2		5.511	[−2.25]	[−1.75]	{0.35}	{0.10}
H^3			1.012	(4.45)	(6.25)	[−0.35]
H^6				1.012	[−0.35]	(6.25)
$H^4(CH_3)$					1.165	{0}
$H^5(CH_3)$						1.165

Table IV. LAME-Optimized Chemical Shifts (ppm; Principal Diagonal Elements) and Proton–Proton Coupling Constants (Hz; Other Elements, ^4J in Brackets, ^5J in Braces) of 2,2-Dimethylmethylenecyclopropane (6) for [$^2H_6$]Benzene Solution

	H^1	H^2	H^3, H^4	H^5, $H^6(CH_3)$
H^1	5.421	1.12	[−1.79][a]	{0.32}
H^2		5.502	[−2.54][a]	{0}
H^3, H^4			0.960	{0}
H^5, $H^6(CH_3)$				1.206

[a] In excellent agreement with the allylic coupling constants reported for 6.[14]

other than methyl or primary or secondary alkyl groups at the ring have been analyzed more rigorously. The allylic coupling constants of such methylenecyclopropanes have been included in a review.[14] In view of the continuing interest in methylenecyclopropanes and the fact that they provide a natural standard of comparison for numerous hetero analogues formally derived therefrom,[15] it seemed highly desirable to determine precise coupling parameters from the proton spectra of simple derivatives. We have therefore reinvestigated the proton spectra of methylenecyclopropane (3) and the methyl-substituted methylenecyclopropanes 4–7.[12]

Results and Discussion

Methyl-Substituted Methylenecyclopropanes 4–7. The results (Tables I–V, Figure 1) clearly show that even at 400 MHz the proton spectra of methyl-substituted methylenecyclopropanes are too complex for a first-order interpretation. This is because virtually all of the theoretically possible couplings must be taken into account in the analysis of the spectra. Only long-range couplings between ring methyl groups (^5J in *cis*-5, *trans*-5, and 7) and between the ring protons and the methyl groups of 6 can be neglected. This results in a maximum number of 15 coupling constants for 2-methylmethylenecyclopropane (4).

The assignment of the vinyl protons was based on the size of the allylic coupling constants in agreement with the relation $|^4J_{cisoid}| < |^4J_{transoid}|$ which holds for three-membered rings with exocyclic carbon-carbon double bonds.[13,14,31] This assignment was corroborated by the observation of the same relation for the coupling constants between the methyl groups and the vinyl protons of 4–7, e.g. $|^5J_{cisoid}| < |^5J_{transoid}|$, in harmony with other systems.[16]

Similarly, the assignment of the ring protons rests upon the magnitude of the (positive) vicinal coupling constants, of which $^3J_{cis}$ is always larger than $^3J_{trans}$ in three-membered rings.[17] The positions of the geminal methyl groups of 7 relative to the ring proton are not reflected in the proton spectrum since the cisoid and the transoid long-range nonallylic coupling constants have the same absolute value: $|^4J_{3,5(cisoid)}| = |^4J_{3,6(transoid)}| = 0.15$ Hz (see below). Therefore, we tentatively base the assignment of the geminal methyl groups of 7 on the small, but albeit significant, shift difference. It can be deduced from the spectra of *cis*-5 and *trans*-5 that a methyl group cis to a vicinal methyl group absorbs at a slightly higher field than trans to this methyl group.

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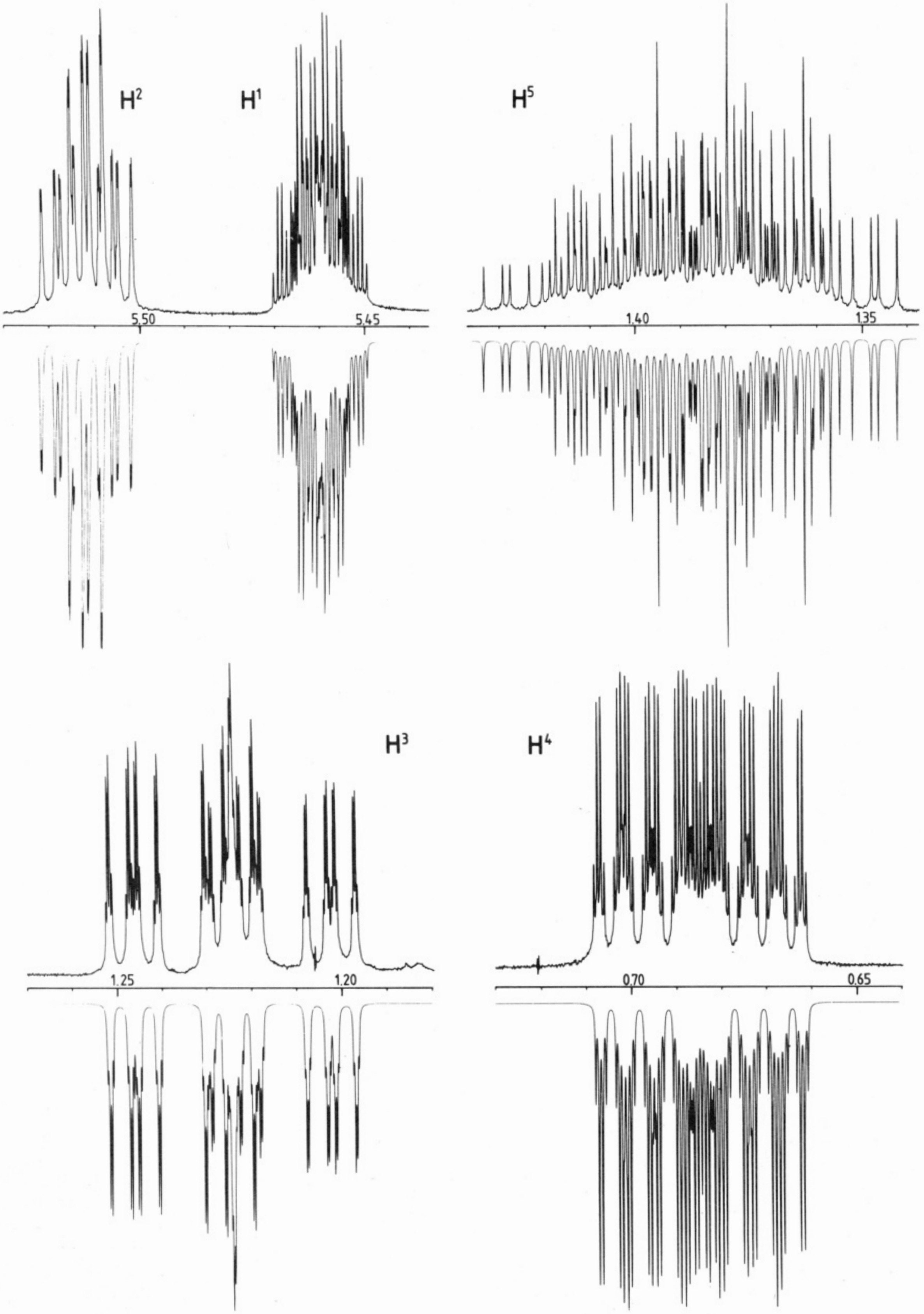

Figure 1. Experimental and computed spectrum (inverted) of 2-methylmethylenecyclopropane (**4**) in [$^2H_6$]benzene. Upper part: multiplets of the vinyl protons (H^1, H^2) and the ring proton H^5. Lower part: multiplets of the ring protons H^3 and H^4. The broadened doublet of the methyl group at 1.137 ppm has been omitted.

As expected, both olefinic-type protons and the methyl groups of **4**–**7** absorb in rather narrow (0.15 ppm) ranges. In contrast, the chemical shifts of the ring methylene and methine protons vary more widely (0.5 ppm). Their absorption frequencies depend upon the methyl substitution pattern at the vicinal ring carbon atom. Thus, comparison of **3**–**5** and **7** reveals that a vicinal *cis*-methyl group produces an upfield shift of about 0.35 ppm while a vicinal *trans*-methyl group shifts the ring proton signal by 0.1–0.2 ppm into the opposite direction.

Table V. LAME-Optimized Chemical Shifts (ppm; Principal Diagonal Elements) and Proton-Proton Coupling Constants (Hz; Other Elements, ^3J in Parentheses, ^4J in Brackets, ^5J in Braces) of 2,2,3-Trimethylmethylenecyclopropane (7) for [$^2H_6$]Benzene Solution

	H^1	H^2	H^3	$H^4CH_3)$	$H^5(CH_3)$	$H^6(CH_3)$
H^1	5.379	1.22	[−1.80]	{0.10}	{0.35}	{0.35}
H^2		5.406	[−2.50]	{0.41}	{0}	{0}
H^3			1.188	(6.40)	[−0.15]	[−0.15]
$H^4(CH_3)$				1.138	{0}	{0}
$H^5(CH_3)$					1.216	{0.15}
$H^6(CH_3)$						1.142

Coupling Constants. Because of the large differences between the chemical shifts of the vinyl and ring protons in the high-field spectra of the methyl-substituted methylenecyclopropanes 4–7, the X approximation is valid. Since the X part of the spectra of *cis*-5 and *trans*-5 is symmetric and since a simultaneous sign change of the allylic couplings does not affect the spectra,[18] the sign of both allylic couplings of *cis*-5 and *trans*-5 was assumed to be negative in agreement with literature data.[14] The vinylic part of the spectra of *cis*-5 and *trans*-5 reveals only the sum of the allylic couplings $|^4J_{\text{cisoid}} + {}^4J_{\text{transoid}}|$. Thus, the individual values given in Tables II and III are only accurate to ±0.3 Hz since their variation by less than 0.3 Hz did not change the spectral region of the ring protons.

The geminal coupling constants of the ring methylene protons of 3 and 4 fall into the range of negative values known for substituted cyclopropanes.[17] The geminal coupling constant of the vinyl protons of the methylenecyclopropanes 3–7 shows the expected small value.[19,20] The sign of that coupling has been determined only for a few exocyclic methylene groups.[13] Its absolute magnitude depended on the size of the ring to which the methylene group was attached. In the few substituted methylenecyclopropanes investigated so far it ranged from undetectably small to 2.5 Hz and was assumed to be negative on the basis of bond angle arguments.[11] Indeed, the proton spectra of the methylenecyclopropanes 3–7 are insensitive to changes of the sign of that geminal coupling. Unfortunately the spectra of 3–5 and 7 are too complex for selective double-resonance experiments, which may afford the relative sign of coupling constants.[21] However, at high field, and neglecting the small transoid coupling between the methyl groups and H^1, the 2,2-dimethylmethylenecyclopropane (6) gives rise to a simple AMX_2 proton spectrum. Therefore, we determined the sign of the geminal coupling constant of the vinyl group for this compound by using the selective spin population transfer technique in the difference mode, which leads to pseudo-INDOR spectra.[22] It was found to be opposite that of the negative allylic couplings and hence positive, in contrast to previous assumptions for similar methylene cyclopropanes.[11] We assume that this also holds for the other methylenecyclopropanes of the present study.

It is interesting, that 4, *cis*-5, *trans*-5, and 7 exhibit significant long-range coupling between the ring protons and the vicinal methyl groups. The sign of both such couplings, $^4J_{\text{cisoid}}$ and $^4J_{\text{transoid}}$, was determined to be negative from the spectra of *trans*-5 and *cis*-5, respectively. Accordingly, the corresponding constants were also assumed to be negative in 4 and 7. The absolute magnitude of this long-range coupling seems to depend upon the substitution pattern of the ring. While the value is certainly less than 0.1 Hz for 6 and of the same magnitude for both $|^4J_{3,5(\text{cisoid})}|$ and $|^4J_{3,6(\text{transoid})}|$ of 7, $|^4J_{\text{cisoid}}|$ is larger than $|^4J_{\text{transoid}}|$ in the methylenecyclopropanes 4, *cis*-5, and *trans*-5. The shape of the signals of the geminal methyl groups of 7 could be optimized only if a small coupling (0.15 Hz) between them is introduced in the computation of the spectrum. Such small ^4J couplings between geminal methyl groups are known for various other systems.[23]

Table VI. LAOCOON III-Optimized Chemical Shifts (ppm) and Proton–Proton and Proton-Carbon-13 Coupling Constants (Hz) of Methylenecyclopropane (3) for [$^2H_6$]Benzene Solution Calculated from the Carbon-13 Satellite Proton Spectrum and the Proton-Coupled Carbon-13 Spectrum of the Ring Methylene Groups (Figure 2)[32]

atoms	shift	coupling constants
H^1, H^2	5.469	$^2J_{1,2} = 1.31$, $^2J_{3,4} = -8.30$
H^3, H^4, H^5, H^6	1.026	$^3J_{3,5(\text{cis})} = 9.94$, $^3J_{3,6(\text{trans})} = 5.78$ $^4J_{1,3(\text{cisoid})} = -1.74$, $^4J_{1,5(\text{transoid})} = -2.48$
$^{13}C(2)$	2.832[a]	$^1J_{H,C(2)} = 161.58$,[b] $^2J_{H,C(2)} = -2.99$ $^3J_{H,C(2)(\text{cis})} = 4.35$, $^3J_{H,C(2)(\text{trans})} = 9.82$

[a] 3.0 ppm in ref 8. [b] 161.5 Hz in ref 8.

Methylenecyclopropane (3). The 56.4-[5] and 400-MHz proton spectrum of methylenecyclopropane (3) consists of a very sharp triplet for the ring protons and a quintet for the vinyl protons. The distances between all vicinal lines correspond to the absolute value of the average of the allylic coupling constants, 0.5 × $|^4J_{\text{cisoid}} + {}^4J_{\text{transoid}}|$. That these two couplings do not have the same magnitude[24] can be deduced from the relative intensities of the lines, which are neither the 1:2:1 expected for the triplet nor the 1:4:6:4:1 expected for the quintet in the case of magnetic equivalence (A_4X_2 system), but rather they are 1.1:1.8:1.1 and 1.1:4.0:5.8:4.0:1.1, respectively. Therefore, methylenecyclopropane (3) resembles the isomeric cyclobutene (8), which exhibits the same symmetry (C_{2v}) and hence is also an AA′A″A‴XX′ spin system. For cyclobutene (8) an unexpected, deceptively simple, two-line proton spectrum has been reported. The spectral parameters for cyclobutene (8) have been determined with the aid of the carbon-13 satellite proton NMR spectra.[25] We used the same method and the proton-coupled carbon-13 spectrum for the spectral analysis of methylenecyclopropane (3) (Table VI, Figure 2).[32] In fact, the absolute value of the difference

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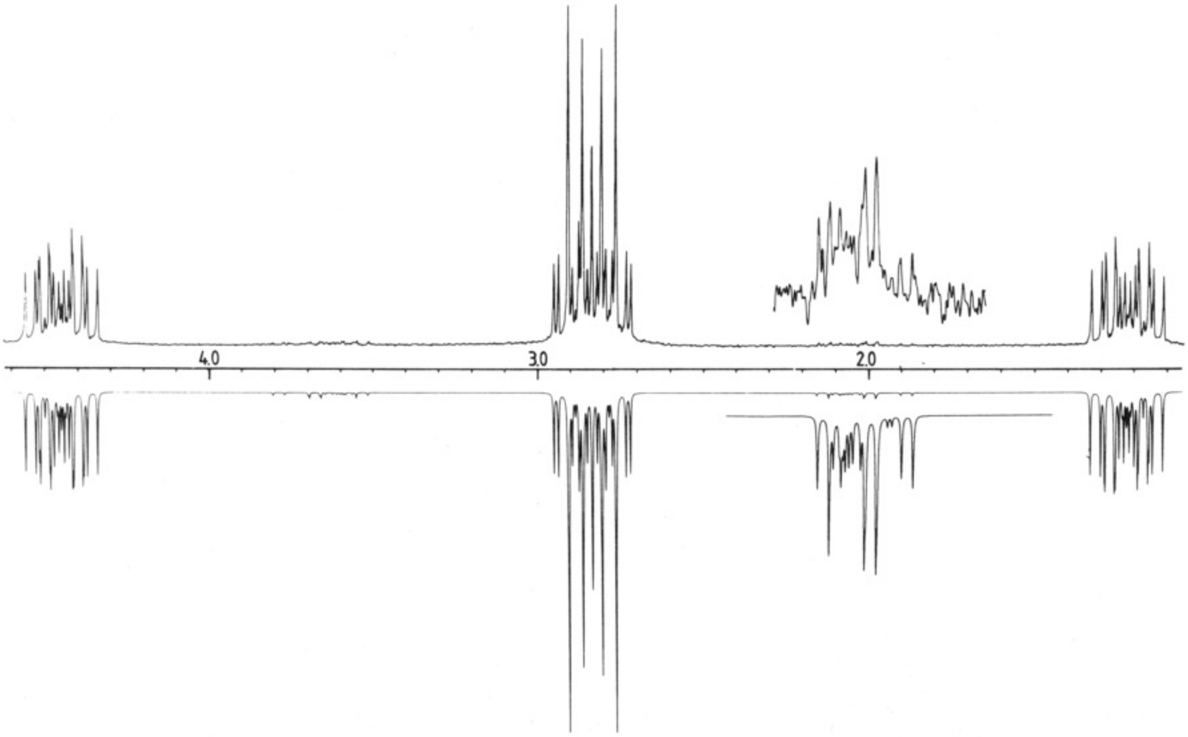

Figure 2. Experimental and computed multiplet (inverted) of the ring methylene group in the proton-coupled carbon-13 NMR spectrum of methylenecyclopropane (**3**). The low-intensity parts of the spectrum have been enhanced by treating the FID with a line-broadening factor of 0.5.

between the allylic coupling constants of **3**, i.e., $|^4J_{\text{cisoid}} - {}^4J_{\text{transoid}}|$, is rather small (0.74 Hz), not far from magnetic equivalence.

Since the spin Hamiltonian for the AA′A″A‴XX′ system[26] cannot be solved, we empirically extended the analysis used for the AA′XX′ system.[27] This was achieved by computing AA′A″A‴XX′ spectra by using different ratios for the six coupling constants. Increasing the difference between the coupling constants of the two sets of isochronous nuclei initially gives rise to a deviation of the triplet and the quintet from the ideal 1:2:1 and 1:4:6:4:1 intensity ratios of the magnetically equivalent case, respectively. Further increase of this difference beyond an approximate threshold leads to a complex, multiline spectrum. The height of this threshold depends upon some of the other coupling constants in the molecule, e.g., the vicinal couplings ($^3J_{\text{cis}}$ and $^3J_{\text{trans}}$) between the ring methylene protons (AA′A″A‴) and the couplings between the vinyl protons (XX′), but is rather insensitive toward changes of the geminal coupling between ring protons. In fact, the latter coupling constant may vary by more than 4 Hz without changing the proton spectrum, including the carbon-13 satellites, and this is also true for the carbon-13 spectrum. On the other hand, the threshold for spectral complexity is rather high if both vicinal couplings between the ring methylene protons are large and, at the same time, the coupling constant between the vinyl protons is small. This case holds for methylenecyclopropane (**3**), which therefore exhibits the seemingly ideal triplet and quintet in its proton spectrum.

In contrast, all three vicinal coupling constants of cyclobutene (**8**) and the difference $|^3J_{1,3} - {}^3J_{1,5}|$ are of similar size and hence would be expected to result in a complex proton spectrum. However, only a two-line spectrum (intensity ratio 1:2) has been reported for **8**.[25] In order to resolve this apparent inconsistency we computed the proton spectrum of **8** using Roberts' spectral parameters[25] and a 0.1-Hz line width. In fact, we obtained a complex spectrum, consisting of two symmetrical groups of lines, the central members of which comprised more than 99.9% of the total intensity and were spread over only about 2 Hz. Thus, a normal resolution and signal to noise ratio inevitably result in the reported deceptively simple two-line spectrum of cyclobutene (**8**).

The proton spectral parameters for methylenecyclopropane (**3**) and the methyl-substituted methylenecyclopropanes **4**–**7** derived in this paper may be useful as an aid for the stereochemical assignments in similar systems, e.g., substituted methylenecyclopropanes and heteromethylenecyclopropanes, provided high field and high resolution are applied as necessary conditions for an appropriate interpretation of the spectra.

Experimental Section

The methylenecyclopropanes **3**–**7** were kindly provided by Dr. Binger, Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim (Ruhr),[28] and were of the following purities (GC): **3**, 99%; **4**, 98.2%; *cis*-**5**, 94.6% containing 3.6% of *trans*-**5**; *trans*-**5**, 94.1% containing 5.1% of *cis*-**5**; **6**, 98.6%; **7**, 95.8%. Samples of 20–30% **3**–**7** in [$^2H_6$]benzene containing 5% of benzene as a secondary standard (at 7.270 ppm relative to internal Me_4Si) and dried over sodium hydride were prepared in 5 mm o.d. NMR tubes by using vacuum line techniques and sealed under 10^{-5} torr.

^{1}H NMR spectra were recorded at 297 K on a Bruker WM 400 spectrometer in the PFT mode (Pw = 20°) by using the deuterium solvent signal as an internal lock. The spectral windows were carefully chosen to ensure that folding did not obscure the spectral region of interest, while at the same time giving a digital resolution in the frequency domain of better than 0.03 Hz. For the determination of coupling constants the Lorentzian-to-Gaussian line-shape transformation was used to enhance resolution. The

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pseudo-INDOR spectra of 6 were obtained by using a 10° observation pulse and a recovery time of 30 s. Eight FID's were acquired with the decoupler set exactly on a given resonance; eight FID's with the decoupler off-resonance were then substracted. This procedure was repeated until an adequate signal-to-noise ratio was achieved.

The natural-abundance ^{13}C spectrum of **3** was obtained in the PFT mode at 100.61 MHz on the same instrument by using quadrature detection. A total of 7200 transients were acquired with a sweep width of 1240 Hz and 16k complex data points, thus leading to a digital resolution of 0.15 Hz in the frequency domain. To improve the shape of the absorption spectrum zero filling up to 32K data points was performed before transforming the FID.

The computations were performed on a Telefunken TR 440 computer in the Rechenzentrum der Universität Würzburg by using the programs LAOCOON III[29] and LAME.[30] The root-mean-square values were as follows: **3**, 0.036; **4**, 0.019; *cis*-**5**, 0.042; *trans*-**5**; 0.045; **6**, 0.010, **7**, 0.038.

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Registry No. **3**, 6142-73-0; **4**, 18631-84-0; *cis*-**5**, 4866-55-1; *trans*-**5**, 5070-00-8; **6**, 4372-94-5; **7**, 34462-28-7.

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(31) **Note Added in Proof**: For 2,2-dimethylmethylenecyclopropane (**6**), the relation $|^4J_{\mathrm{cisoid}}| < |^4J_{\mathrm{transoid}}|$ has now been established by Nuclear Overhauser difference spectroscopy.

(32) **Note Added in Proof**: The analysis of the carbon-13 satellite spectrum of the ring methylene group of methylenecyclopropane in [$^2H_6$]benzene by W. Herrig has led to essentially the same results: $\delta_{1,2} = 5.44$, $\delta_{3-6} = 1.03$; $^2J_{1,2} = 1.6 \pm 0.8$, $^2J_{3,4} = -9.7 \pm 0.5$, $^3J_{3,5} = 9.93 \pm 0.02$, $^3J_{3,6} = 5.77 \pm 0.02$, $^4J = -1.74 \pm 0.02$, -2.49 ± 0.02 (Herrig, W., Diploma Thesis, University of Cologne, 1972). We thank Professor Günther, University of Siegen, West Germany, for bringing these data to our attention.

Syntheses of 2-Carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone, a Potential Precursor of Macrocyclic Azulene Analogues, and (*Z*)- and (*E*)-14-Carbethoxy-2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]fulvenes[1]

Vijay K. Sharma, Hooshang Shahriari-Zavareh, Peter J. Garratt,* and Franz Sondheimer†

Department of Chemistry, University College London, London WC1H OAJ, England

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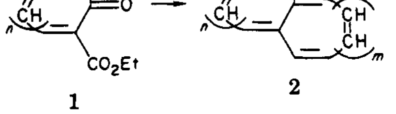
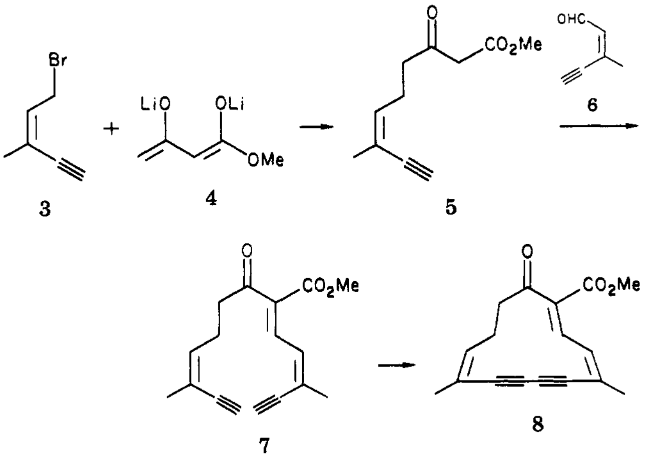
The synthesis of 2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**15**), a potential precursor of macrocyclic azulene analogues, and its elaboration into (*E*)- (**19**) and (*Z*)-14-carbethoxy-2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]fulvene (**20**) is reported. The ^1H NMR spectrum of **15** is interpreted to indicate that in the average conformation the C-12,13 double bond is not coplanar with the ring, and a reappraisal of the conformation of 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone (**16b**) is made. The [13]fulvenes **19** and **20** show little or no paratropicity and serve as model systems for the estimation of paratropicity in **15** and related systems.

The first synthesis of macrocyclic analogues of naphthalene in which both rings are larger than benzene were reported in 1975.[2,3] These successes focussed attention on the possibility of preparing macrocyclic analogues of azulene[4] and octalene,[5] and we devised an approach to the azulene-type systems which involved the annelation of a 2-substituted [4*n* + 1]annulenone. It was envisaged that the combined functionality supplied by the ketone group and the 2-substituent would allow the fabrication of the second ring, and a *β*-keto ester was chosen as the target compound, allowing the transformation **1** → **2**.[6] We now report the synthesis of 2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**15**), a 2-substituted [4*n* + 1]annulenone and a potential precursor of azulene type systems, and describe some of its chemistry.



1 **2**

Scheme I



Our initial approach was based on our recently reported synthesis of 5,10-dimethyl-6,8-bisdehydro[13]annulenone,[7]

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† Deceased, February 11, 1981.

(1) Unsaturated Macrocyclic Compounds. 131. For part 129, see: Taylor, R. J. K.; Sondheimer, F. *J. Org. Chem.* **1981**, *46*, 4594. For part 130, see: Cresp, T. M.; Sondheimer, F. *Tetrahedron Lett.* **1982**, *23*, 1731.

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