mediate values are expected if rotamer averaging takes place or if the rotamer is skewed relative to its natural preference. Clearly, such couplings provide useful structural information. For example, for Ile-9, the χ_1 torsion angle is either 60° or –60° (60° based on HNHB[6] and HN(CO)HB[7] experiments), and χ_2 is 180°. As can be seen from Table I, and as expected on the basis of a statistical search of the protein data bank,[8] χ_2 is 180° for most Ile residues in the protein–peptide complex. A large number of similar dihedral constraints can be derived from the $^3J_{CC}$ couplings measured for other residues. Two-bond J_{CC} couplings may yield additional information, analogous to $^2J_{CH}$ couplings,[9] but they tend to be quite small; the largest measured value in calmodulin was 1.9 Hz.

The method presented here demonstrates a convenient way for obtaining information on the conformation of methyl group containing side chains in proteins. The spectrum can be recorded in a 2D fashion but also is easily extended into a 3D experiment with a "constant-time" ^{13}C evolution period[10] by replacing the first and second T periods by $T + t_2$ and $T - t_2$, respectively. The information provided in the present experiment complements that of other approaches which measure long-range ^1H–^{13}C couplings.[9,11]

Supplementary Material Available: A table with 104 multiple bond ^{13}C–^{13}C couplings, derived from the spectrum shown in Figure 2 (2 pages). Ordering information is given on any current masthead page.

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Is 2,3,5,6-Tetrakis(methylene)bicyclo[2.2.0]hexane the Product of Photolyzing 7-Oxa[2.2.1]hericene?

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Whether the ground state of 1,2,4,5-tetrakis(methylene)benzene (TMB) biradical (**1**) is a singlet or a triplet is of considerable interest.[1–5] This molecule belongs to the class of "disjoint"[6–11]

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Table I. Optimized Geometrical Parameters

TMBCH[a] (3)			7-oxa[2.2.1]hericene (2)		
parameter[b]	4-21G	6-31G**	parameter[b]	4-21G	6-31G**
R_{12}	1.539	1.526	R_{12}	1.533	1.527
R_{23}	1.499	1.490	R_{23}	1.502	1.499
R_{14}	1.598	1.573	d_{14}	2.309	2.300
R_{27}	1.312	1.317	R_{28}	1.314	1.319
$R_{1,11}$	1.076	1.082	$R_{1,12}$	1.074	1.079
$R_{7,12}$	1.073	1.076	$R_{8,13}$	1.072	1.075
$R_{7,13}$	1.073	1.076	$R_{8,14}$	1.072	1.075
∠11,1,4	124.3	123.6	∠12,1,7	117.5	117.2
∠11,1,2	118.7	117.7	∠12,1,2	116.1	116.1
∠2,1,6	111.8	114.5	∠2,1,6	106.1	107.2
∠7,2,1	133.8	133.7	∠8,2,1	126.4	126.2
∠7,2,3	134.3	134.7	∠8,2,3	128.3	128.6
∠1,2,3	91.8	91.6	∠1,2,3	105.3	105.2
∠2,1,4	88.2	88.4	∠2,1,7	99.2	98.9
∠2,1,4,5	111.9	114.6	∠2,1,4,5	111.8	113.0
∠7,2,3,4	177.8	117.4	∠8,2,3,4	-179.0	-178.5
			∠1,7,4	97.2	97.4
			∠7,1,2,3	33.7	33.8
			R_{CO}	1.200	1.181

[a] TMBCH: 2,3,5,6-tetrakis(methylene)bicyclo[2.2.0]hexane. [b] The numbering of atoms is given in structures **2** and **3**.

biradicals which are expected on the basis of Hückel MO theory to have close-lying singlet and triplet states. Both semiempirical[1] and ab initio calculations[2,3] predict a singlet ground state for **1** with the triplet 5–7 kcal/mol higher at the highest level of theory applied.[3] However, a recent UV–vis and ESR study on the photoproduct of 7-oxa[2.2.1]hericene (**2**) favored a triplet ground state for TMB.[4]
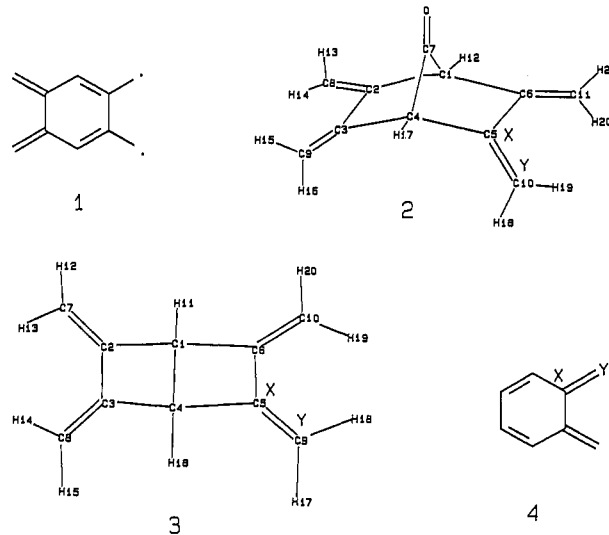
More recently, Berson et al.[5] reported experimental studies on the same photoreaction and concluded that the carrier of the ESR and UV–vis signals, reported in ref 4, is not the same species. By photolyzing 2,3-($^{13}CH_2$)$_2$-labeled **2**, they observed a new ^{13}C NMR signal at 113 ppm which is 8 ppm from that of the precursor, and its intensity increase was matched quantitatively by the intensity decrease of the precursor signal. On the basis of comparison of the chemical shift of the new signal with those of the singlet biradicals, e.g., 3,4-bis(methylene)furan (102 ppm)[12] and 3,4-bis(methylene)thiophene (105 ppm),[13,14] and the agreement between the calculated values[3] of λ_{max} and ϵ for the $^1A_g \rightarrow {}^1B_{3u}$ transition of the singlet TMB and the observed results,[5] they concluded that a kinetically stable singlet TMB is responsible for

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Table II. Calculated Absolute NMR Shieldings[a]

| basis | 7-oxa[2.2.1]hericene (2) | | | tetrakis(methylene)bicyclo[2.2.0]hexane (3) | | | o-xylylene (14) | | |
	energy[b]	X	Y	energy	X	Y	energy	X	Y
6-31G**	−479.153 92	64.04	98.26	−384.371 44	56.77	98.03	−307.553 27	66.02	91.43
6-31+G**	−479.168 94	60.83	100.21	−384.382 94	53.67	100.37	−307.563 57	63.65	93.74
6-311G**	−479.250 62	47.19	86.12	−384.439 60	40.94	86.08	−307.608 44	51.35	79.57

[a] Calculated with the GIAO method at the SCF/6-31G** optimized geometries; unit is ppm. [b] Total SCF energy; unit is hartree.

both the NMR and UV–vis signals. However, the possibility that the new NMR signal originates from 2,3,5,6-tetrakis(methylene)bicyclo[2.2.0]hexane (3) was not excluded completely, although the explanation of the UV–vis signal seems less satisfactory in the latter case.[5]

To help clarify the identity of the photoproduct, we carried out theoretical calculations on the structures and magnetic shielding tensors for the vinyl carbons X and Y of 2, 3, and o-xylylene (4). It would be more conclusive to calculate the NMR shieldings of TMB, too; however, the program for open-shell molecules is not available at present. Nevertheless, on the basis of the structural and electromagnetic environmental similarities, it is reasonable to expect that the chemical shift of the methylene carbon of 4 is close to that of the singlet TMB.

All the structures were fully optimized at the SCF level using the 4-21G[15] and 6-31G** [16a] basis sets. The results for 2 and 3 are given in Table I. Note that the $C_2C_1C_6$ bending and C_2-$C_1C_4C_5$ dihedral angles of 3 vary significantly ($\approx 3°$) with basis sets. This indicates that the molecule is highly strained. Since higher angular momentum polarization functions give better descriptions for strained molecules, the results obtained with the 6-31G** basis are expected to be more reliable. Consequently, the NMR shielding calculations were carried out at the 6-31G** geometries by the gauge-independent atomic orbital (GIAO) method[17] at the SCF level using the 6-31G**, 6-31+G**, and 6-311G** basis sets.[16] The program TX90[18] was used for all the calculations.

Table II contains the calculated absolute NMR shieldings and SCF energies. With all three basis sets, the methylene carbon shieldings of 2 and 3 differ by less than 1 ppm. This indicates that if 3 were produced in the photolysis of 2, its methylene ^{13}C signal would be indistinguishable from the precursor signal. On the other hand, the NMR shielding of the methylene carbon of 4 is calculated to be lower than that of 2 by 6.83 (6-31G**), 6.47 (6-31+G**), and 6.55 (6-311G**) ppm. This difference corresponds well with the observed signal of the photoproduct of Berson et al. Therefore, it is reasonable to believe that the photoproduct is in a singlet state and has a structural unit similar to 4.

Presumably due to the high reactivity, there have been no reports of ^{13}C NMR measurements for 3 and 4. For 2, the ^{13}C NMR shifts of atoms X and Y are reported[19] to be 142.5 and 103.8 ppm, respectively. The difference, 38.7 ppm, agrees very well with our calculated results, 34.22 (6-31G**), 39.38 (6-31+G**), and 38.93 (6-311G**) ppm. In fact, in previous studies[17b] in this laboratory, a chemical shift difference as small as 0.7 ppm between the para and meta carbons in styrene has been correctly reproduced by using the 6-31G(d) basis set.

In summary, this theoretical study provides convincing evidence supporting the conclusion of Berson et al. that the new ^{13}C NMR signal observed at 113 ppm is not that of 3. The fact that 2,3,5,6-tetrakis(methylene)bicyclo[2.2.0]hexane was not produced in the photolysis of 7-oxa[2.2.1]hericene may be explained by the calculated molecular structures. To produce 3, the distance be-

tween C_1 and C_4 has to decrease from 2.30 Å to 1.57 Å, which invokes a strong strain effect, and therefore, this mechanism is unfavorable kinetically.

Intracluster Ion–Molecule Reactions within Ethylene–Methanol Heteroclusters

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Recent studies on the properties, structure, and reactivities of molecular clusters contribute to an understanding of the reaction dynamics lying between the gaseous and condensed phases.[1-3] Apart from the numerous investigations of the structure of the ions formed in gas-phase ion–molecule association reactions, there are few reported cases of chemical reactions taking place within the heterocluster ion itself.[4-6]

In this study we have investigated the $(C_2H_4)_n(CH_3OH)_m$ heterocluster systems to look for new intracluster ion–molecule reactions occurring within the ionized clusters and to elucidate reactive pathways not ordinarily found in bimolecular ion–molecule collisions. The molecular beam apparatus used in this work has been described previously.[7] Neutral heteroclusters are generated by expanding a gas mixture (6% C_2H_4; 0.03–0.6% CH_3OH) seeded in 4.5 atm of He through an 800-μm pulsed nozzle. Ions formed by the electron impact are accelerated in a double electrostatic field to 1.1 keV and directed through a 1-m-long flight tube. The mass spectrum is recorded by a transient digitizer coupled with a microcomputer.

Figure 1 displays the mass spectra taken at different mixing ratios of ethylene/methanol (E/M) of 10/1 and 100/1. Though $E_nM_mH^+$ ions show only small contributions compared to the corresponding unprotonated species in the 10/1 ratio, the same ions are now substantially increased in intensity when they are formed at the 100/1 ratio. This observation is easily explained assuming that the proton is bound to a methanol molecule in $E_nM_mH^+$ ions due to the large difference between the proton affinities[8] of CH_3OH (8.03 eV) and C_2H_4 (7.10 eV). A similar result has also been found in a study of the dissociation of mixed ammonia–acetone cluster ions.[9,10] In the 10/1 ratio, the pro-

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