rotation–conformational adjustment of 18-crown-6 is unique. It would be interesting to look for cases where the crown could rotate without conformational change. It would also be of interest to see if the large cyclic alkanes (which are known from ^{13}C CP/MAS studies to have mobility in the solid phase[29–31]) undergo similar kinds of motion, exchanging CH_2 groups or larger units.

Acknowledgment. G.W.B. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for continued financial support via an operating grant.

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Alkali Metal Atom Induced Acetylene–Vinylidene Rearrangement: Matrix Isolation ESR Study

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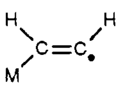
Abstract: Interactions between alkali metal atoms and acetylene molecules cocondensed in argon matrices were examined by ESR spectroscopy. The following are shown: (1) No reaction occurs between alkali metal atoms in the ^2S ground state and acetylene molecules, but the side-on π complexes are formed between alkali metal atoms in the ^2P excited state and the acetylene molecules. (2) Subsequent exposure of the π complex to light corresponding to the $\pi \rightarrow \pi^*$ transition in the acetylene moiety results in its isomerization to the vinylidene form $M{:}C{=}CH_2$. The g tensors, the proton, and the alkali metal–atom hyperfine coupling tensors of the observed π and vinylidene complexes and the ^{13}C hfc tensor of the Li–acetylene π complex were determined. In the case of the Na/acetylene/argon system, only the vinylidene complex was observed due to coincidence of the 3s $\rightarrow$ 3p transition of Na atom and the $\pi \rightarrow \pi^*$ transition of the π complex.

Introduction

The acetylene–vinylidene isomerization process has been the subject of many theoretical studies.[1] It is now reasonably well agreed that vinylidene, the simplest form of carbene $H_2C{=}C{:}$, exists as a bound molecule. The ground state of vinylidene lies ~44 kcal/mol above that of acetylene, however, and the barrier for the vinylidene-to-acetylene rearrangement is only 2–4 kcal/mol. The situation for the corresponding anionic system differs significantly. The isomerization process between the acetylene anion and vinylidene anion has been shown to be thermoneutral; a barrier of 40 ~ 50 kcal/mol has been computed for the rearrangement, however.[2,3] Experimental values determined by Ervin, et al.,[4] based on the photoelectron spectroscopy of vinylidene anions, are in excellent accord with these theoretical predictions.

The effect of interacting alkali metal atoms on the acetylene–vinylidene rearrangement has also been examined theoretically.[3,5,6] Of the three possible equilibrium structures, **1**, **2**, and **3**, it has



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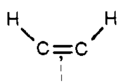

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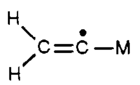

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been concluded that (1) the σ-bonded structure **1** is not a bound state, (2) the π-bonded state **2** is weakly bound (by several kcal/mol), and (3) the Li–vinylidene structure **3** is also an equilibrium state; it is slightly less stable than **2** (by several kcal/mol), and there exists a high barrier (40 ~ 50 kcal/mol) against the isomerization process between the two structures.

Manceron and Andrews[7] detected, in their matrix isolation IR study, the formation of the π complex **2** between the Li atoms and acetylene molecules cocondensed in argon matrices at 15 K in total accord with the theoretical result briefed above. In structure **2** the C–H bonds are bent away from the metal atom as depicted. Based on the relative intensities of the symmetric and antisymmetric C–H stretching modes, they estimated the CCH angle of 140°, also in an excellent accord with the theoretical value (139°).[5,6] The corresponding π complexes were not observed with heavier alkali metal atoms (Na, K, Cs); these metal atoms catalyzed intermolecular hydrogen transfer within hydrogen-bonded acetylene molecules, however.[8]

We had earlier conducted an ESR study of argon matrices containing Na atoms and acetylene molecules, and observed photoinduced formation of Na–acetylene complexes.[9] The ESR spectrum of the complex was characterized by small hyperfine coupling (hfc) interaction with one ^{23}Na nucleus, and large, essentially isotropic hfc interaction with two equivalent hydrogen nuclei, and was hence assigned to the complex of the vinylidene structure **3**. The assignment appeared to be in contradiction with the theoretical results[3,5,6] reported afterward. As will be shown later, the issue was unsettled further by INDO molecular orbital calculations predicting that the isotropic components of the hfc tensors of the Na and hydrogen nuclei of the π complex **2** (with bent acetylene) would be very similar to those of the vinylidene form **3**. A thorough reexamination of the alkali metal atom–acetylene interactions by ESR thus appeared clearly in order.

We report here the result of such (re)examination of the alkali atom (Li, Na, K)–acetylene interactions in argon matrices. We

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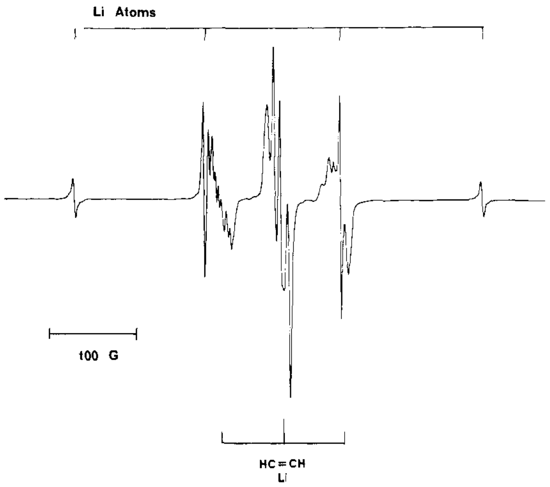

Figure 1. The ESR spectrum of the Li/acetylene (1%)/Ar system. The sharp quartet due to Li atoms and the 1:2:1 triplet due to the Li–acetylene complex are observed.

managed to obtain much better resolved ESR spectra of the complexes, enabling us to determine the anisotropic components of the hfc tensors and also the spectra of ^{13}C labeled complexes. The study has revealed (1) that no reaction occurs between alkali metal atoms in the ^2S ground state and acetylene molecules, but that side-on π complexes are formed between alkali metal atoms in the ^2P excited state and the acetylene molecules, and (2) that subsequent exposure of the π complex to light corresponding to the $\pi \rightarrow \pi^*$ transition in the acetylene moiety results in its isomerization to the vinylidene form $M{:}C{=}CH_2$. In the case of Na/acetylene/argon system, only the vinylidene complex was observed due to coincidence of the $3s \rightarrow 3p$ transition of Na atom and the $\pi \rightarrow \pi^*$ transition of the π complex.

Experimental Section

The liquid helium cryostat–ESR spectrometer system, which would enable trapping of vaporized metal atoms in inert gas matrices and examination of the resulting matrix by ESR, has been described earlier.[10] In the present series of experiments, the Na and Li atoms were generated from resistively heated stainless steel tubes (280 °C for Na, and 550 °C for Li), and potassium atoms were generated by reacting molten Li metal with KCl in a stainless steel tube maintained at 370 °C (following the scheme given in ref 8). The alkali atoms thus generated were trapped in argon matrices containing controlled amounts (0.5~2 mol %) of acetylene. In each experiment approximately 5 mmol of gaseous mixture was deposited in a period of 1 h; the concentration of metal atoms was estimated to be 0.1 mol %.

The ESR spectrometer used was an IBM Instruments Model 200D, X-band spectrometer, and the microwave frequency locked to the sample cavity was typically 9.410 GHz. For photoirradiation of the matrix, a high pressure Xe–Hg lamp (Oriel, 1 kW unit) was used. The light beam was passed through a water filter and a broad-band (±50 nm) interference filter of choice, and was focused on the cold finger ~40 cm away. The ESR spectra were obtained with the matrices maintained at ~4 K.

Research grade argon (Matheson), acetylene (Matheson), and ^{13}C labeled acetylene (Cambridge Isotope, enrichment >99%) were used without further purification. Na and Li metals were obtained from Alfa Products, and ^6Li (enrichment >95%) metal was obtained from U.S. Services, Inc.

Spectra and Assignments

Li–Acetylene Interaction. The ESR spectrum of Li atoms ($2s^1$) isolated in an argon matrix was studied earlier by Jen et al.[11] The spectrum is a widely spaced, sharp quartet due to the isotropic hfc interaction with the ^7Li nucleus ($I = {}^3/_2$, $A_{iso} = 149$ G). An argon matrix in which Li atoms and acetylene molecules had been cocondensed appeared bright green, and showed the ESR spectrum shown in Figure 1. The signals due to isolated Li atoms are recognized as indicated. The remaining groups of signals comprise

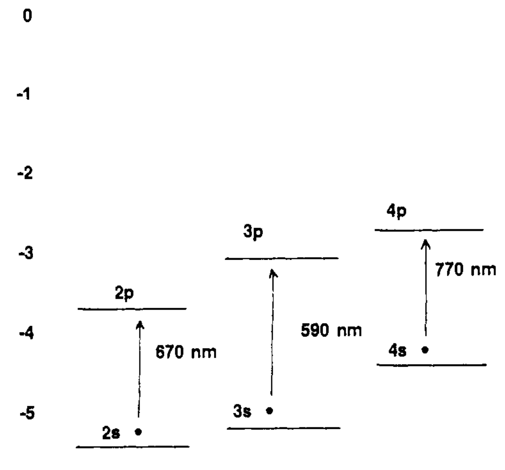

Figure 2. The valuence s and p orbital levels of alkali metal atoms.[12]

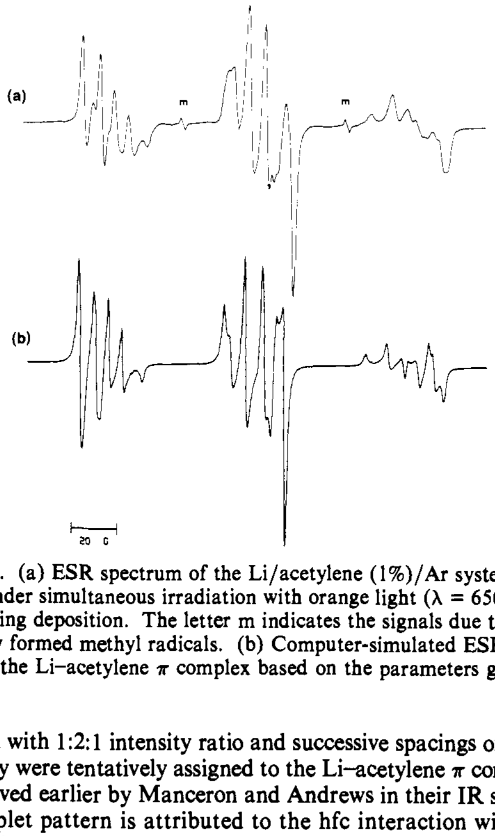

Figure 3. (a) ESR spectrum of the Li/acetylene (1%)/Ar system prepared under simultaneous irradiation with orange light (λ = 650~700 nm) during deposition. The letter m indicates the signals due to inadvertently formed methyl radicals. (b) Computer-simulated ESR spectrum of the Li–acetylene π complex based on the parameters given in Table I.

a triplet with 1:2:1 intensity ratio and successive spacings of ~65 G. They were tentatively assigned to the Li–acetylene π complex, **2**, observed earlier by Manceron and Andrews in their IR study.[7] The triplet pattern is attributed to the hfc interaction with the two equivalent hydrogen nuclei. The hfc interaction with the ^7Li nucleus would account for the quadruplet splittings with successive spacings of ~7 G discernible in the central component of the triplet. The presence of an excessive number of signals in the lowest-field component of the triplet and incongruous broadening of signals in the highest-field component hampered further analysis of the spectrum.

Let us define the direction parallel to the C–C bond of the complex as the x-axis, and the direction perpendicular to the molecular plane as the z-axis (as in Figure 11). The extremely small ^7Li hfc tensor immediately rules out a complex in which the unpaired electron is localized in a sp_y hybridized orbital of the Li atom pointing away from the ligand. The most likely SOMO (semi-occupied molecular orbital) of the π complex is that representing migration of the unpaired electron in the Li p_x orbital into the π_y^* orbital of the acetylene moiety. The formation of the π complex from the Li atom in its ground state ($2s^1$) is thus symmetry forbidden; the formation with the Li atom in the excited $2p^1$ state is allowed. We envisaged that some of the adverse

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Table I. g Tensors and the ^{1}H and the Metal Atom Hfc Tensors (G) of Alkali Metal Atom–Acetylene and Vinylidene Complexes[a]

		$HC{=}CH$ Li	$Li{:}C{=}CH_2$	$Na{:}C{=}CH_2$	$HC{=}CH$ K	$K{:}C{=}CH_2$
g tensor	x	2.0008	2.0008	2.0014		
	y	2.0029	2.0023	2.0023	2.0023	2.0023
	z	2.0032	2.0031	2.0032		
A(H)	x	71.0	59.0	62.0		
	y	66.5	57.0	59.0	73.0	58.5
	z	62.0	55.0	58.5		
A(M)	x	−5.5	−5.0	−12.5		
	y	−6.5	−5.7	−12.5	−3.3	−2.7
	z	−9.0	−6.5	−13.0		
$A_{iso}(^{13}C)$		74 ± 1				

[a] For the K complexes only the isotropic values were assessed. The uncertainties are ±0.0003 for the g tensor and ±0.5 G for the hfc tensors. The x, y, z axes are defined in Figure 11.

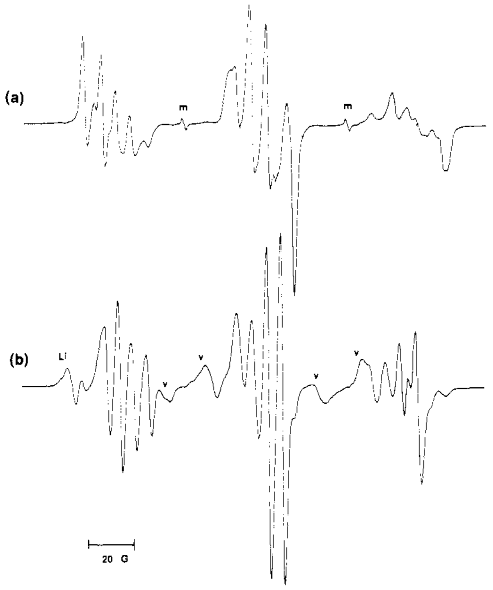

Figure 4. (a) ESR spectrum of the Li/acetylene (1%)/Ar system prepared under simultaneous irradiation with orange light (λ = 650∼700 nm) during deposition (same as Figure 3a). The letter m indicates the methyl radical signals. (b) ESR spectrum of the Li/acetylene (1%)/Ar system prepared under simultaneous irradiation with blue light (λ = 450 ± 50 nm) during deposition. The letter v indicates signals due to vinyl radicals.

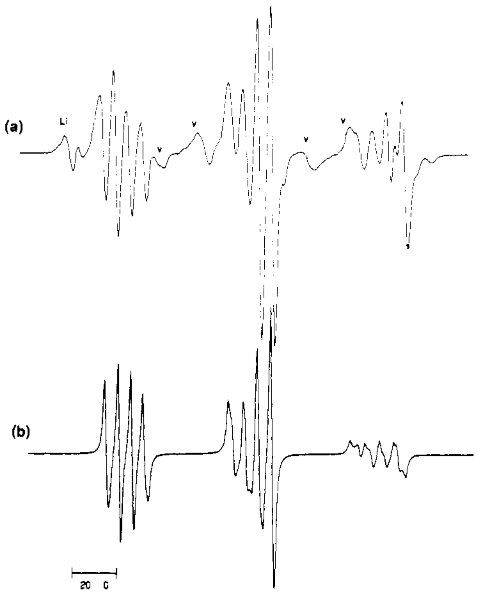

Figure 5. (a) ESR spectrum of the Li/acetylene (1%)/Ar system prepared under simultaneous irradiation with blue light (λ = 450 ± 50 nm) during deposition (same as Figure 4b). The letter v indicates signals due to vinyl radicals. (b) Computer-simulated ESR spectrum of $Li{:}C{=}CH_2$ based on the parameters given in Table I.

features of the observed spectrum were associated with inhomogeneous matrix effect caused by quenching of thermally activated reaction process. Depicted in Figure 2 are the valence ns and np orbital levels of the Li, Na, and K atoms.[12] Accordingly the Li/acetylene (1%)/Ar matrix was prepared with simultaneous irradiation of the cold finger with orange light (λ = 650∼700 nm) during deposition. Figure 3a shows the ESR spectrum of the resulting matrix. The Li atom signals are absent, and the signals due to the complex are seen with much improved resolution.

Starting from the model hfc tensors based on the SOMO given by the INDO calculation for the π structure, **2**, and through successive trial-and-error adjustments, the g tensor, the ^{7}Li hfc tensor, and the hfc tensors of the two protons (including their orientations relative to the g tensor) were determined via spectral simulation.[13] The results are given in Table I. The computer simulated powder pattern based on these parameters is shown in Figure 3b. The details of the process are given in the Discussion section. The assignment of the spectrum in Figure 3a to the Li–acetylene π complex is thus strongly substantiated.

No efficacious effect resulted when the Li/acetylene (1%)/Ar system prepared in the dark was post-exposed to orange light (λ = 650∼700 nm). However, most interestingly, exposure of these matrices to more energetic light (λ = 450∼600 nm) resulted in gradual but complete conversion (in ∼20 min) of the ESR spectrum to that of the second complex. Deposition of the matrix with simultaneous irradiation with blue light (λ = 450 ± 50 nm) produced the matrix exhibiting the "pure" spectrum of the second complex. Figure 4 compares the spectrum of the first π complex and that of the second complex observed from the Li/acetylene (1%)/Ar system prepared under simultaneous irradiation with blue light. The broad signals indicated by letter v are due to photoinduced vinyl radicals $H_2C{=}CH$ resulting from intermolecular hydrogen-transfer reactions within hydrogen-bonded acetylene molecules.[8,9] These signals became dominant when the acetylene concentration was increased (to 2%) as expected.

It is evident that the spectrum of the second complex is also characterized by the hfc interactions with one ^{7}Li nucleus and two equivalent hydrogen nuclei, and their magnitudes are very close to those of the first complex. The noticeable differences are a slight decrease of the proton coupling constants and perhaps a significant reduction in the anisotropy of the ^{7}Li hfc tensor. The second spectrum was tentatively assigned to the Li–vinylidene complex, **3**. Again starting from the model hfc tensors based on the SOMO given by the INDO calculation and through trial-and-error adjustments, the g tensor, the ^{7}Li hfc tensor, and those of the two equivalent hydrogen nuclei were determined (see Table I). Figure 5 compares the observed spectrum of $Li{:}C{=}CH_2$ and the computed powder pattern based on these parameters. Details of the assignment process are given in the Discussion section. The agreement between the observed and simulated spectra is rea-

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(13) Kasai, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 5950.

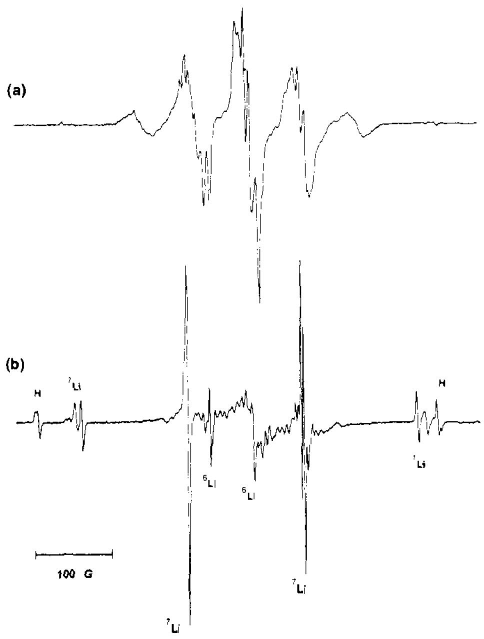

Figure 6. (a) ESR spectrum of the Li/$^{13}C_2H_2$ (1%)/Ar system prepared under simultaneous irradiation with orange light (λ = 650~700 nm). (b) ESR spectrum of the Li/$^{13}C_2H_2$ (1%)/Ar system prepared under simultaneous irradiation with blue light (λ = 450 ± 50 nm). The signals due to Li atoms (split by site effect) and hydrogen atoms are seen as indicated.

sonable and is a strong support of the assignment of the second spectrum to the vinylidene complex.

In order to obtain further substantiation of the assignments, we repeated the experiment using ^{13}C labeled acetylene. The spectrum observed from the Li/$^{13}C_2H_2$ (1%)/Ar system prepared under simultaneous irradiation with orange light (λ = 650~700 nm) is shown in Figure 6a. The overall quintet pattern with the binomial intensity ratio and successive spacings of ~70 G is readily accounted for by the hfc constants of the two protons of the π complex determined already and additional hfc interaction of the same magnitude with two ^{13}C nuclei ($I = {}^1/_2$). From the positions of the outermost components of the quintet, the isotropic component of the ^{13}C hfc tensor was determined as 74 ± 3 G. The presence of two equivalent carbons and a nontrivial unpaired electron density in their valence s orbitals (as attested by the large, essentially isotropic ^{13}C hfc tensor) are in unequivocal support of the π complex **2**, with bent C–H bonds.

When the ^{13}C labeled matrix discussed above was subsequently irradiated with blue light, the spectrum of the π complex disappeared, but no spectrum of comparable intensity appeared in its place. When observed with a higher spectrometer gain, many weak signals were observed scattered within and beyond the range of the spectrum of the vinylidene complex generated from the normal acetylene. Figure 6b shows the spectrum of the Li/$^{13}C_2H_2$ (1%)/Ar system prepared under simultaneous irradiation with blue light (λ = 450 ± 50 nm) and observed with a higher gain (×8). Signals due to hydrogen atoms and remnant Li atoms (including those of naturally abundant ^{6}Li atoms) are conspicuously recognized as indicated. The weak signal strength and complexity of the spectrum of the ^{13}C labeled vinylidene complex, Li:$^{13}C{=}^{13}CH_2$, are attributed to broadening and splittings of the pattern by ^{13}C hfc tensor(s) of extreme anisotropy. When the SOMO contains, in an LCAO description, only a 2p orbital of a carbon but not its 2s orbital, the ^{13}C hfc tensor of the carbon is known to be extremely anisotropic.[14] The SOMO of the vinylidene complex, **3**, is of this category. Because of the weakness and complexity of the pattern, and the presence of overlapping signals due to metal atoms, efforts to assess the ^{13}C hfc tensor of the vinylidene complex were aborted. The difficulty was not resolved when the attempt was repeated using the ^{6}Li isotope with enrichment >95%. The nuclear magnetic moment of ^{6}Li is ca. one-fourth of that of ^{7}Li. Further details on the analysis of the ^{13}C hfc tensors of both the π and vinylidene complexes are given in the Discussion section.

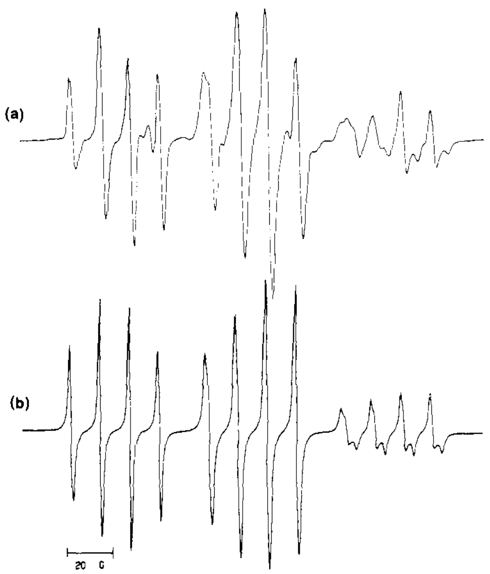

Figure 7. (a) ESR spectrum of the Na/acetylene (1%)/Ar system observed after irradiation with yellow light (λ = 600 ± 50 nm). (b) Computer-simulated ESR spectrum of Na:C=CH$_2$ complex based on the parameters given in Table I.

Na–Acetylene Interaction. The ESR spectrum of Na atoms ($3s^1$) isolated in an argon matrix was also studied earlier by Jen et al.[11] The spectrum is a widely spaced, sharp quartet due to the isotropic hfc interaction with the ^{23}Na nucleus ($I = {}^3/_2$, A_{iso} = 330 G). An argon matrix in which Na atoms and acetylene molecules had been cocondensed appeared dark red, and showed only the ESR signals due to isolated Na atoms. Thus, in contrast to the Li–acetylene situation, there is no spontaneous formation of a complex between Na and acetylene in an as-prepared argon matrix.

Photoirradiation of the Na/acetylene (1%)/Ar system with yellow light (λ = 600 ± 50 nm, covering the Na 3s → 3p transition) for 8 min resulted in total disappearance of the Na signals, and appearance of strong multiplets centered about the position of g = 2.00. Figure 7a shows the photoinduced spectrum thus obtained. The triplet-of-quartet spectrum with the respective spacings of ~58 G and ~12 G is that reported earlier.[9] The current spectrum is of much improved resolution, however. The hfc interaction of ~58 G with two equivalent protons is nearly the same as that determined for the Li–vinylidene complex. The ^{23}Na hfc constant of ~12 G is roughly twice that of the ^{7}Li hfc constant determined for its vinylidene complex, the ratio being close to that of the hfc constants of isolated ^{23}Na and ^{7}Li atoms (330 G versus 149 G). Also the spectrum remained unaltered when the matrix was irradiated with more energetic light (λ = 450 ± 50 nm). It is thus strongly implicated that the spectrum observed here is that of the Na–vinylidene complex. The alkali metal atom–vinylidene complex is essentially a charge-transfer complex $M^+{:}C^-{=}CH_2$. A minimal effect is expected on its SOMO if the Li^+ cation of the complex is replaced with Na^+. The most likely scenario is that Na–acetylene π complexes are formed as the result of the 3s → 3p transition of Na atoms, but are immediately isomerized to the vinylidene form by the ensuing radiation.

Starting from the model hfc tensors based on the SOMO given by the INDO calculation of the vinylidene complex, and via iterative spectral simulations, the g tensor, the ^{23}Na hfc tensor, and the hfc tensors of the two protons of the vinylidene complex were determined. The results are shown in Table I. Figure 7b is the computer simulated spectrum based on these parameters.

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(14) Kasai, P. H. *J. Phys. Chem.* **1982**, *86*, 3684.

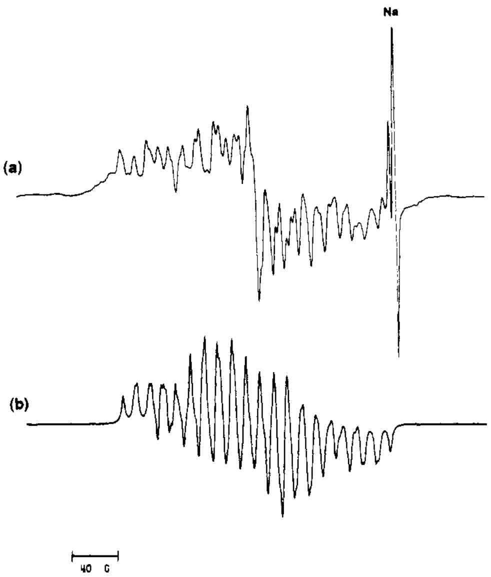

Figure 8. (a) ESR spectrum of the Na/$^{13}C_2H_2$ (1%)/Ar system observed after irradiation with yellow light (λ = 600 ± 50 nm); 64 scans were accumulated, each scan made with an 8-fold spectrometer gain. The sharp central peak is due to organic radicals of ubiquitous source. (b) ESR spectrum simulated based on the parameters of the nonlabeled Na:C=CH$_2$ complex and the "model" ^{13}C hfc tensors based on the SOMO given by an INDO calculation (see text for detail).

The agreement between the observed and simulated spectra is considered reasonable.

Further substantiation of the assignment was obtained by repeating the experiment using ^{13}C labeled acetylene. When the Na/$^{13}C_2H_2$ (1%)/Ar matrix was irradiated with yellow light (λ = 600 ± 50 nm), the signals due to Na atoms disappeared completely, but no signals of comparable intensity appeared in their steads. Examination with a higher spectrometer gain revealed the appearance of many weak signals scattered within and beyond the range of the spectrum photoinduced from Na and normal acetylene. Figure 8a shows the result of accumulating 64 scans, each scan made with an 8-fold spectrometer gain. The broad signals in the background are believed to be due to vinyl radicals. The INDO calculation of the Li–vinylidene complex placed the unpaired electron density of 0.66 in the p_y orbital of the central carbon and 0.14 each at hydrogen 1s orbitals. The ^{13}C hfc tensors of the complex can thus be estimated with some certainty. Figure 8b shows the simulated spectrum based on the parameters of Na–vinylidene determined already and the additional "model" hfc tensors of A_y = 66 G, A_z = A_x = 3.5 G for the central ^{13}C, and A_x = A_y = A_z = 10.0 G for the terminal ^{13}C. The overall spread and characteristic shapes of individual signals of the observed and computed spectra are clearly in accord. Direct assessment of the ^{13}C hfc tensors through the iterative simulation process was not attempted, however. Further details of the assignment of the normal and ^{13}C labeled Na–vinylidene complexes are presented in the Discussion section.

K–Acetylene Interaction. There are two major isotopes of potassium, ^{39}K and ^{41}K, with the respective natural abundances of 93 and 7%, and $I = {}^3/_2$ for both nuclei. The ESR spectrum of K atoms (4s^1) isolated in an argon matrix had also been studied by Jen et al.[11] They did not show the spectrum, but reported the presence of several sets of quartets due to matrix site effects. An argon matrix in which K atoms and acetylene had been cocondensed appeared sky-blue, and, with matrices containing 1 or more mol % acetylene, irradiation resulted in disappearance of the K atom signals and appearance of strong signals due to vinyl radicals. The result is consistent with the reported propensity of heavier alkali metal atoms to induce intermolecular hydrogen atom transfer between hydrogen-bonded acetylene molecules.[8]

Figure 9a shows the ESR spectrum observed from the K/acetylene (0.5%)/Ar system deposited in the dark. The signals are mostly due to isolated K atoms as indicated (with the measured A_{iso} of ~90 G and ~50 G for ^{39}K and ^{41}K, respectively). The signals are split into multiplets due to severe matrix site effects. Irradiation of the matrix with red light (λ = 750 ± 50 nm) for 8 min resulted in diminution of the K atom signals and conspicuous appearance of a triplet of quartets with the respective spacings of 73 G and 3.3 G (Figure 9b). On subsequent irradiation with yellow light (λ = 600 ± 50 nm) for 8 min, the initially formed triplet of quartets disappeared, and the second set with slightly reduced spacings, 59 G and 2.7 G, appeared. The two sets of triplets of quartets are shown in Figure 10 in an expanded scale. Very few signals due to vinyl radicals appeared during the process.

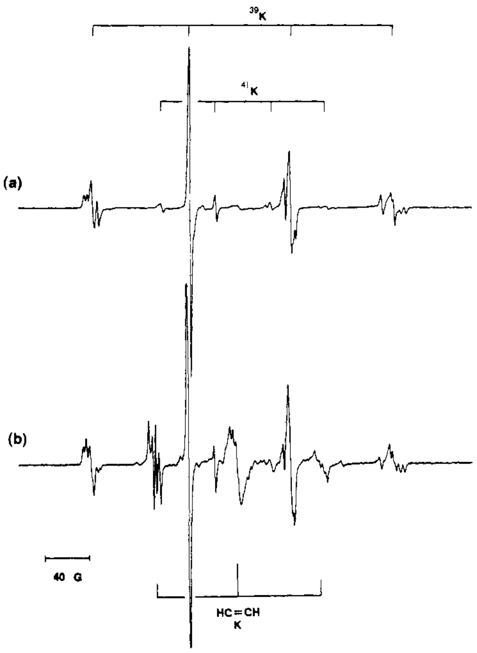

Figure 9. (a) ESR spectrum of the K/acetylene (0.5%)/Ar system observed as prepared. The signals due to isolated K atoms are indicated. (b) ESR spectrum of the same matrix observed after photoirradiation with red light (λ = 750 ± 50 nm). The photoinduced triplet is attributed to the K–acetylene π complex.

The photoinduced changes observed above can be best accounted for by the formation of the K–acetylene π complex on excitation of the K 4s → 4p transition, and its isomerization to K–vinylidene on exposure to more energetic light (λ = 600 ± 50 nm). The hfc constant of two equivalent protons in each complex is indeed very close to that of the corresponding complex observed in the Li–acetylene system. The magnitude of the ^{39}K coupling in each complex is also that expected from the ^{7}Li coupling constant of the corresponding Li complex reduced by the ratio of the coupling constants of the isolated metal atoms (149 G and 90 G).

Discussion

Li–Acetylene and Li–Vinylidene Complexes. It has been established that the INDO molecular orbital method yields the hfc tensors of an open-shell system with reasonable reliability.[15] We hence performed the INDO calculations for the Li–acetylene π complex and Li–vinylidene complex based on the equilibrium structures given by the ab initio calculations.[3,5,6] The equilibrium structures assumed and the SOMO's of the respective complexes thus obtained are depicted in Figure 11. The unpaired electron densities in the relevant atomic orbitals are also shown. Both structures may be grossly viewed as charge-transfer complexes, the bent acetylene anion interacting side-on with the Li cation, and the vinylidene anion interacting end-on with the cation. In both cases the Li atom is at the nodal plane of the SOMO; its hfc tensor should hence be small. Based on the known hfc constant

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[15] See, for example: Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

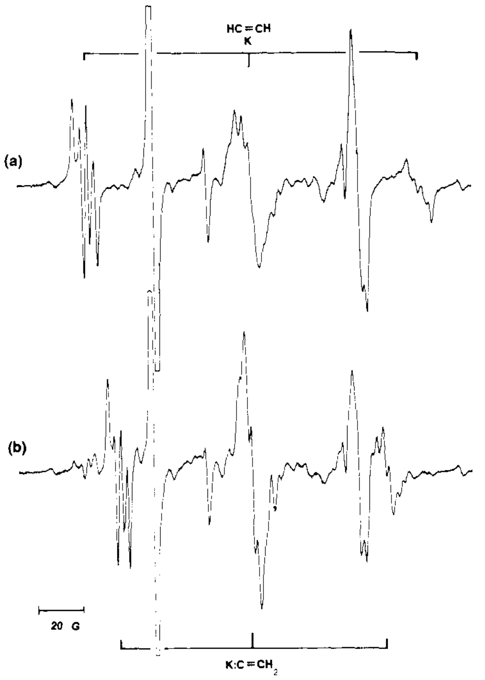

Figure 10. (a) ESR spectrum of the K–acetylene π complex observed from the K/acetylene (0.5%)/Ar system after irradiation with red light (λ = 750 ± 50 nm). (b) ESR spectrum of the K–vinylidene complex observed after subsequent irradiation with yellow light (λ = 600 ± 50 nm).

Table II. Principal Elements of A_{dip}, Computed and Observed (in Parentheses) Values (G)

		z	x	y	θ,[a] deg
HC═CH Li	A_{dip}(H)	−4.0	+8.0	−4.0	±26
		(−4.5)	(+4.5)	(0.0)	(±30)
	A_{dip}(^{7}Li)	−1.3	+1.3	0.0	
		(−2.0)	(+1.5)	(+0.5)	
Li:C═CH$_2$	A_{dip}(H)	−2.0	+3.8	−1.8	±20
		(−2.0)	(+2.0)	(0.0)	(±10)
	A_{dip}(^{7}Li)	−1.3	+1.1	−0.2	
		(−0.8)	(+0.8)	(0.0)	

[a] θ gives the direction of the x axis of the hfc tensor relative to the direction of g_x within the xy plane (see Figure 11).

of isolated hydrogen atoms (505 G), both SOMO's predict an isotropic hfc constant of ~70 G with the two protons. The basic aspects of these SOMO's should change little, if the Li atom is replaced by Na. Our earlier assignment[9] of the spectrum observed from the Na/acetylene/Ar system to the Na–vinylidene complex based only on the presence of two equivalent protons, and the magnitudes of the isotropic components of the proton and ^{23}Na hfc tenors, was clearly premature.

The hfc tensor of a magnetic nucleus consists of the isotropic component, A_{iso}, and the dipolar term, A_{dip},[16] as follows:

$$\mathbf{A} = A_{iso} + A_{dip} \tag{1}$$

where

$$A_{iso} = g_e\beta_e g_n\beta_n(8\pi/3)|\phi(0)|^2$$

$$A_{dip} = g_e\beta_e g_n\beta_n\left\langle \phi\left|\frac{3\cos^2\alpha - 1}{r^3}\right|\phi\right\rangle$$

Here ϕ is the SOMO, r is the distance between the unpaired electron and the magnetic nucleus, and α is the angle between r and the magnetic field. A_{dip} is thus usually given in the tensor form and its element A_{ij} (where $i, j = x, y, z$) may be given as follows:

$$A_{ij} = g_e\beta_e g_n\beta_n \int \frac{1}{r^5}(3ij - \delta_{ij}r^2)\phi^2\,d\tau \tag{2}$$

Here x, y, z, and r are the values given by the position of unpaired electron measured from the magnetic nucleus. Equation 2 has been evaluated analytically for a proton hfc tensor of a π radical many years ago.[17] Numerical integration of eq 2 in terms of a SOMO of the LCAO form is straightforward.

We performed the numerical integration of eq 2 for the Li–acetylene π and Li–vinylidene complexes considering only the atomic orbitals depicted in Figure 11, and using the Slater orbitals for each AOs. The results are summarized in Table II. Since A_{dip} is a traceless tensor, the isotropic component, A_{iso}, should be equal to the "average spacing" of the hyperfine structure in question. The model proton and ^{7}Li hfc tensors of the complexes may then be constructed by combining the computed A_{dip} and the experimentally observed A_{iso}, assuming the appropriate sign for the latter. The large A_{iso} of ~60 G observed for the protons of both complexes must surely be positive; they are too large to be ascribed to a negative spin density induced by polarization of the σ bonding electrons. The A_{iso} of the ^{7}Li nucleus was assumed to be negative. In both cases, the Li atom is at the nodal plane of the respective SOMO's, and participation of its p orbitals in the SOMO is small.[18]

As stated in the preceding section, starting from the model hfc tensors constructed above, the g tensors and the hfc tensors of the complexes were determined through the iterative simulation process. The results are given in Table I. From the experimentally determined $A_{iso} = (A_x + A_y + A_z)/3$ and the known coupling constants of isolated atoms (505 G for H, and 149 G for ^{7}Li), the spin densities in the relevant s orbitals were assessed as given in Figure 11. Assuringly the theoretical values are in reasonable agreement with the experimental values. The isotropic ^{13}C coupling constant of 74 G determined for the ^{13}C labeled Li–acetylene π complex (Figure 6a) yields, based on the atomic value of $|\phi(0)|^2_{C,2s}$,[19] the carbon 2s density of 0.054, perhaps fortuitously, in exact agreement with the theoretical value.

The individual principal elements of A_{dip} in the finally chosen hfc tensors are shown in Table II for comparison with the starting values. Understandably the theoretical A_{dip} served only as a crude model; it did predict correctly the magnitudes of the tensors and signs of individual elements and facilitated the assignment process.

It has been shown that, for a radical with a nondegenerate ground state $|0\rangle$, deviation of the g term from the spin only value g_e = 2.0023 is given as follows:[20]

$$g_i - g_e = -2\lambda\sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_0} \tag{3}$$

Here i (=x, y, z) represents a principal axis of the **g** tensor, L_i the orbital angular momentum operator, and λ the one-electron spin–orbit coupling constant. The summation is performed for all the excited states. In evaluating eq 3 in terms of LCAO–MO's, only one-centered integrals may be retained, and for each atomic integral the spin–orbit coupling constant of the particular atom is used. In the Li complexes concerned here, only the carbon atoms have the spin–orbit coupling constant of consequence. It follows immediately that, for both complexes, $g_y \simeq 2.0023$. Also, for the complexes, the closest lying excited state that would give nonvanishing matrix elements in eq 3 is the lowest unoccupied orbital, the π_z^* orbital of the C═C sector. A negative g shift ($g < 2.0023$) is hence predicted in the x direction. Again, for both complexes, other excited states of significance relating to eq 3 are those involving the σ electrons of the (:)C═C sector. A positive g shift is hence predicted in the z direction. The observed **g** tensors are in accord with these predictions.

Na–Vinylidene Complex. As stated already, replacing the Li atom in the Li–vinylidene complex with the Na atom should

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(16) See, for example: Ayscough, P. B. *Electron Spin Resonance in Chemistry*; Methuen: London, 1967; pp 58–104.

(17) McConnell, H. M.; Strathdee, J. *Mol. Phys.* **1959**, *2*, 129.

(18) Adrian, F. J.; Jette, A. N. *J. Chem. Phys.* **1984**, *81*, 2415.

(19) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(20) Pryce, M. H. L. *Proc. Phys. Soc. London, Sect. A* **1950**, *63*, 25.

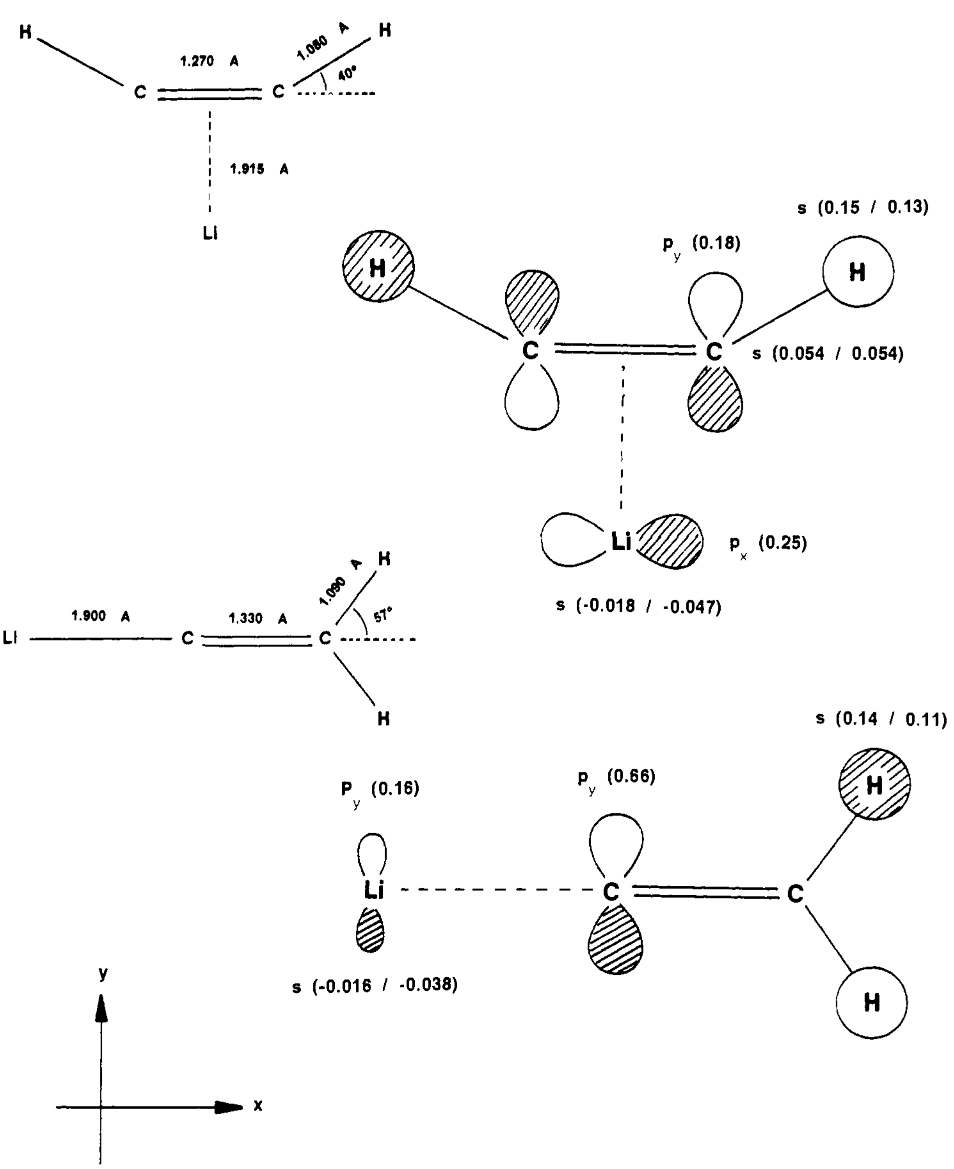

Figure 11. The structures assumed for INDO calculations of the Li–acetylene and Li–vinylidene complexes, and the SOMO's of the complexes given by the calculations. The spin densities in relevant atomic orbitals are given inside the parentheses; the second values, when given, are those determined from the observed hfc tensors.

produce little change in its SOMO. The analysis of the ESR spectrum (Figure 7a) was hence attempted starting with the model hfc tensors based on the SOMO of the Li–vinylidene complex (Figure 11) with an appropriate scaling of the metal hfc tensor. The spin Hamiltonian parameters thus determined through the iterative simulation process are given in Table I. The simulated spectrum proved to be extremely sensitive in its details to various parameters. Some of the variances between the observed and simulated spectra (Figure 7) are suspected to be due to a small ^{23}Na nuclear quadrupole term.

The ^{13}C hfc tensor due to a unit spin density in a 2p orbital of carbon is known. Its principal elements are $A_{\parallel} = 104$ G, and $A_{\perp} = 5$ G, where $A_{\parallel}$ is the coupling constant in the direction parallel to the p orbital.[14] It is also known that, when there is a unit spin density in a p_π orbital of a given carbon, an isotropic coupling constant of ~ -14 G is induced for the ^{13}C nucleus directly bonded to the first carbon.[21] The ^{13}C hfc tensors used in the simulation of the ^{13}C labeled Na–vinylidene complex (Figure 8b) were those modeled after these tensors adjusted for the spin density of 0.66 at the central carbon. The agreement between the observed and simulated spectra is marginal; the assumed ^{13}C hfc tensors, however, correctly produced the extended range of the spectrum due to the isotropic substitution, the overall envelop of the pattern, and characteristic shapes of individual signals. Also the spectral simulation for a mixture of 1 part of the normal and 10 parts of the ^{13}C labeled Na–vinylidene complexes indicated that the signal strength of the labeled complex would be weaker by two orders of magnitude, as experienced indeed.

Alkali Atom Induced Acetylene–Vinylidene Isomerization. It has been shown earlier that, when metal atoms of low ionization potential and molecules with some electron affinity are cocondensed in an argon matrix, an electron transfer between them can be induced by mild radiation, and the resulting metal cations and molecular anions are effectively isolated from each other.[10] When Na atoms are used as the electron donors, for example, yellow light (λ = 600 ± 50 nm) covering the Na 3s → 3p transition was sufficient and minimum-required to induce the electron transfer, and the ESR spectrum of the resulting anion radicals is totally free from the hyperfine structure due to the Na cation. Also it has been shown experimentally[22] and theoretically[2,3] that the acetylene molecule has a negative electron affinity. We hence conclude that the alkali metal atom–acetylene π complexes observed in the present study are not the product of the photoinduced

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[21] See, for example: Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972; pp 125–128.

[22] Dressler, R.; Allan, M. *J. Chem. Phys.* **1987**, *87*, 4510.

electron transfer process, but are the result of spontaneous interaction between acetylene molecules and alkali metal atoms in their excited ^2P states. Formation of a certain amount of the Li–acetylene complex in the dark is attributed to a much higher temperature required for vaporization of Li atoms, and much greater mobility of the latter in a fluid surface layer of the matrix during deposition.

The ESR spectrum of well-annealed Li–acetylene complex was thus observed when the matrix was simultaneously irradiated with orange light ($\lambda = 650{\sim}700$ nm) during deposition, and the K–acetylene complex was formed only after irradiation of the matrix with red light ($\lambda = 750 \pm 50$ nm). In both cases the isomerization to the vinylidene form was observed to occur on exposure to light of $\lambda \leq 600$ nm. The situation in the Na/acetylene/argon system must be that the π complexes are formed upon irradiation of the matrix with yellow light ($\lambda = 600 \pm 50$ nm), but are immediately isomerized to the vinylidene form by the ensuing radiation.

As stated earlier, the alkali metal atom–acetylene complex is essentially a charge-transfer complex, a bent acetylene anion interacting side-on with an alkali metal cation. The photoenergy of $\lambda \leq 600$ nm (= 48 kcal/mol) required for its isomerization to the vinylidene form is in excellent agreement with the theoretically predicted barrier height of $40{\sim}50$ kcal/mol for the process.[3,5,6] The electronic transition involved here must be that which correlates to the $\pi_z \rightarrow \pi_y{}^*$ transition of the acetylene moiety. The $\pi \rightarrow \pi^*$ transition of an isolated acetylene occurs at ~240 nm.[23] A rather large red-shift of the transition to ~600 nm in the π complex is not unreasonable in view of the distortion and the interaction involving the $\pi_y{}^*$ orbital.

Acknowledgment. My thanks to S. Sakai and M. T. Nguyen for stimulating discussions of the subject.

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(23) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; D. Van Nostrand: New York, 1967; p 611.

A New Definition of Functional Groups and a General Procedure for Their Identification in Organic Structures

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Abstract: Functional groups (FGs) have always been used to describe structures and reactivities of organic molecules, therefore their univocal identification is important. Current approaches are often subject to limits and errors, using descriptions that are either too approximated or too rigid. A new definition, and the corresponding search procedure, based on the calculation of a molecular descriptor is introduced and applied to some molecules of different complexity. Results show a consistent set of FGs for each structure. They are divided into two classes—first level FGs and second level FGs—that describe interactions either among atoms (first level) or among groups of atoms (second level).

Introduction

The recognition of functional groups (FGs) in organic molecules is important both for their handling (e.g. in organic reactivity modeling) and for their storage and retrieval in reaction databases. FG identification is also important in all computer programs for organic synthesis planning, both those using a database of reactions and those using a mechanicistic approach (in this last case the recognition can be implicit).

The inspection of an organic structural formula by a chemist involves the direct and efficient perception of the molecular characteristics through a mental mechanism that is a complex collaborative interaction between symbolic and graphical recognition and memory correlation. A similar operation carried out by a computer requires great care in the exact definition of the object to be perceived and in the realization of a general procedure that can be applied to any molecule.

There are two possible approaches to the problem: (1) the choice of a set of fundamental FGs that permits the recognition of the FGs in a given molecule via an accurate comparison between its atomic groups and the FG set;[1,2] (2) the definition of a set of rules, listing the necessary requisites of an FG, that can be applied to a given molecule furnishing its FGs.

The first approach is the most similar to the chemist's style: his/her knowledge is represented by the chosen FG set and his/her mental process is simulated by the comparison procedure. Both the chemist and the machine will take advantage of the exact definition of the FGs, thus the analysis will be fast and reliable. On the other hand, both the chemist and the machine will suffer the limited number of FGs in the set and, for some particular structures, the FG recognition could be partial or erroneous. All the current methods for FG identification are of this type.

The second approach will be generally applicable (if the rules are sufficiently comprehensive), permitting the identification of uncommon and even new FGs; but it will suffer a longer search time and, mainly, the possible insertion of apparently similar atomic groups into different FG classes.

The procedure being presented is of the second approach type that guarantees a greater potential applicability. In addition the procedure is based on the calculation of a molecular descriptor that is a number and not a descriptive representation; therefore it can be an effective aid in determining a correct FG classification, useful in describing and handling molecules. Eventually it is in accord with our approach to synthesis design[3] that does not use a priori defined FGs. The main results are as follows: (1) the possibility of identifying FGs in any molecule, regardless of its complexity; (2) the independence of the FGs from an a priori

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(1) Esack, A.; Bersohn, M. A Program for Rapid and Automatic Functional Group Recognition. *J. Chem. Soc., Perkin Trans. I* **1974**, 2463–2470. For an original approach to the representation of organic reactions and reaction centers see also: Fujita, Shinsaku Description of Organic Reactions Based on Imaginary Transition Structures. 9. Single-Access Perception of Rearrangement Reactions. *J. Chem. Info. Comput. Sci.* **1987**, *27*, 115–120 and references cited therein.

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(3) Baumer, L.; Sala, G.; Sello, G. Organic Synthesis Planning: Fundamental Principles in a New Approach (Lilith). *Anal. Chim. Acta* **1990**, *235*, 209–214.