the formation of the triflate derivative (vertex 6 in *nido*-$B_{10}H_{14}$) suggests that the arylation, alkylation, and triflation reactions all proceed from a common high-energy intermediate which is produced only in noncoordinating solvents. As shown in eq 2, the boranocation, $B_{10}H_{13}^+$, is a presentable candidate for this intermediate.

The addition of three protons to the *closo*-$B_{10}H_{10}^{2-}$ might produce an open $B_{10}H_{13}^+$ cage having but 22 skeletal electrons, such as (**A**), which could rearrange to an isomer with 24 skeletal electrons (**B**) by conversion of an empty localized skeletal orbital to an empty terminal boron orbital by an internal hydride migration (Scheme I). The cationic B-6 of **B** then attacks available electron sources without great discrimination (Scheme II).

The proposed generation and reactions of a boranocation are without precedent, but the experimental results reported here fall into the same category and require an unusual explanation. Work continues with this fascinating chemistry.

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Supplementary Material Available: Tables of position and thermal parameters, bond lengths and angles, and crystallographic data for **1** and **3** (12 pages); listing of observed and calculated structure factors for **1** and **3** (15 pages). Ordering information is given on any current masthead page.

Observation of Fluorescence Emission from Solutions of C_{60} and C_{70} and Measurement of Their Excited-State Lifetimes

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Since the early stage of research on bulk C_{60} and related fullerenes, much interest has been shown in the optical spectra of these species in an effort to elucidate the electronic structures and their implication in the chemistry and physics of the fullerene family. Absorption spectra of C_{60} solutions in the UV–visible range were obtained by many groups[1–4] and show good agreement among them. A typical absorption spectrum shows a very weak absorption band between 430 and 620 nm, probably due to a forbidden transition, and a series of stronger absorption peaks at shorter wavelengths. The absorption spectrum of C_{70} shows weak and broad absorption around 470 nm and further stronger absorption features at shorter wavelengths.[2–4] However, no emission spectrum for C_{60} in room temperature solution has been reported to date, although in low-temperature solids weak fluorescence has been observed.[5,6] Things have been mostly similar in the case of C_{70},[7] but room temperature fluorescence spectra from hexane and benzene solutions were reported to be observed as broad emission between 650 and 725 nm.[7] The fluorescence was found to be very weak, with a quantum yield of about 8.5×10^{-4}. Transient absorption measurements of these fullerenes yielded indirect estimates for the lifetime of the excited singlet state C_{60} as 1.2 ns[8] or 0.65 ns,[9] and that for C_{70} as 0.67 ns.[10] Lifetimes as short as 33 ps for C_{60} and 0.11 ns for C_{70} have also been suggested.[11]

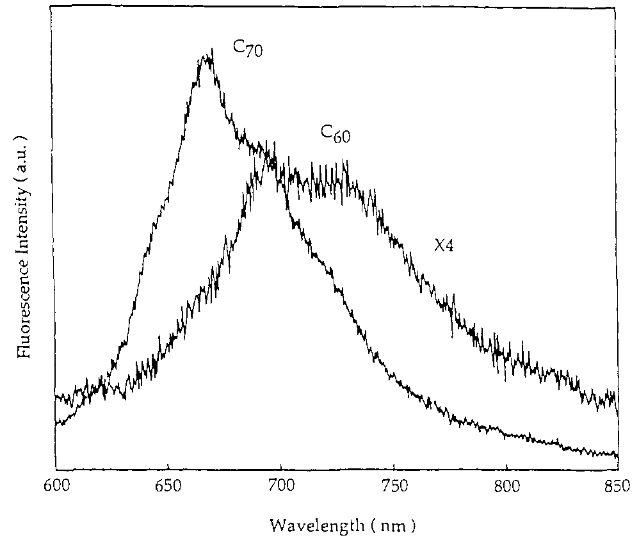

Figure 1. Fluorescence emission spectra of C_{60} and C_{70} in toluene at room temperature (excitation wavelength = 525 nm).

We report here the first observation of very weak fluorescence emission from highly purified samples of both C_{60} and C_{70} in toluene and in benzene at room temperature. The fullerenes were produced by the contact-arc method and purified by now-standard procedures.[12] FT-IR, Raman, and ^{13}C NMR spectroscopy as well as HPLC and mass spectrometry were employed to identify the species. For C_{60}, the sample purity was estimated to be 99.5% or higher from mass spectrometric measurement. The purity of the C_{70} sample was also very high, ca. 98%, and the only detectable impurity was C_{60}.

Figure 1 shows fluorescence emission spectra of C_{60} and C_{70} in toluene following excitation at 525 nm. The emission spectra were obtained on a SLM-Aminco spectrofluorometer. The concentration of C_{60} in solution was 1×10^{-3} M. The C_{70} solution was diluted to match the optical density of C_{60} at the excitation wavelength. Emission from C_{60} solution is broad but matches very well the 20 K luminescence spectrum of solid C_{60} film deposited on CaF_2,[5] and especially the luminescence spectrum of polycrystalline solid at 5 K.[6] In the 20 K luminescence study, Whetten, Diederich, and co-workers observed 1420-cm^{-1} spacings in their absorption spectrum. This was compared to the energy of one quantum of the totally symmetric (A_g) pentagonal pinch mode[14] in the ground state, 1469 cm^{-1}, reduced by only 5% presumably due to a geometry similar to that of the ground state. In their emission spectra they also observed single vibronic structure with

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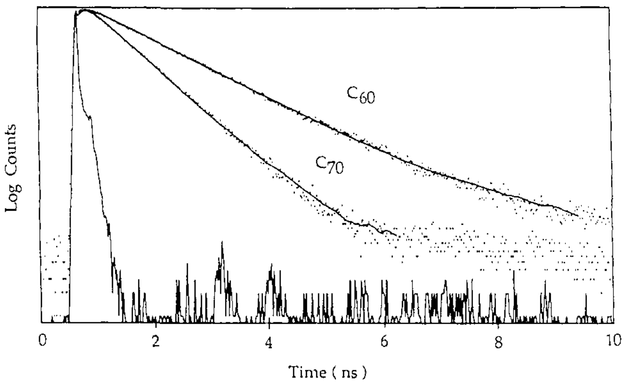

Figure 2. Log–linear plot of fluorescence decay curves for C_{60} and C_{70} in toluene at room temperature. Shown in the short-time region is the instrument response function for our time-correlated single photon counting scheme.

1400 ± 100 cm^{-1} spacings, which most likely was a manifestation of the 1469-cm^{-1} mode.

The splitting between the two major peaks in our C_{60} spectrum (Figure 1) is determined to be about 490 cm^{-1}, which is comparable to the one for the solid sample at 5 K.[6] We believe that this corresponds to the energy of a vibrational quantum for the other totally symmetric (A_g), Raman active breathing mode in the ground state,[14] 496 cm^{-1}. In fact, the emission spectra from 20 K film also seem to reveal the same feature, although it is not explicitly mentioned (upper spectrum of Figure 3 of ref 5).

The fluorescence spectrum of C_{70} shows a maximum at significantly shorter wavelengths near 15 000 cm^{-1}. Here again, polycrystalline solid at 5 K gives a spectrum similar to that of our room temperature sample, the only difference being the relative peak heights.[6] The recently reported emission spectrum of C_{70} at 77 K shows a much better resolved fine structure,[7] but our room temperature solution spectrum clearly gives a rough envelope of it. It is estimated that when calibrated against the same optical density, the fluorescence intensity of C_{60} at the peak is about 5 times weaker than that of C_{70}. The fluorescence quantum yield for the latter has been estimated to be about 8.5×10^{-4} by comparison with the tetracene fluorescence at 540 nm.[7] We thus expect the fluorescence quantum yield of C_{60} in room temperature solution to be about 2×10^{-4}, which is in good agreement with a conservative estimate for the lower bound of 10^{-4}.[13]

Time-correlated single photon counting (TCSPC) detection was carried out to determine the lifetimes of the singlet states of C_{60} and C_{70} in solution. The laser source consists of a CW mode-locked Nd:YAG laser and a cavity-dumped dual-jet dye laser. The dye laser pulses with a pulse energy of 10–18 nJ at 570–605 nm, and a repetition rate of 3.8 MHz was monitored by a real-time autocorrelator. The pulse width was measured to be 1 ps. With the use of a microchannel plate photomultiplier tube (Hamamatsu Model R2809), it was possible to obtain an instrument response function as short as 25 ps. To eliminate rotational contribution to the fluorescence lifetime, the fluorescence emission from the sample was detected at the magic angle with respect to the excitation polarization, and a polarization scrambler was put in front of the monochromator. Toluene and benzene of HPLC grade were used as solvents. To check the possibility of impurity fluorescence, these pure solvents alone (without C_{60} or C_{70}) were excited at 587 nm and monitored over 600–850 nm. No fluorescence was observed in this wavelength region. All the fullerene solutions were degassed by a freeze–pump–thaw cycle three times before each use.

The fluorescence decay curves for both C_{60} and C_{70} in toluene are shown in the semilog plot of Figure 2. It is clearly seen that each shows a single exponential decay. By a deconvolution technique with nonlinear curve fitting, the lifetimes are determined to be 1.17 ± 0.02 ns for C_{60} and 0.66 ± 0.02 ns for C_{70}. The calculated curves based on these lifetimes are also shown in the figure. The fluorescence lifetimes of undegassed samples were measured as well and found to be shorter by 5–6% for both C_{60} and C_{70}. Lifetimes were also measured as a function of concentration. There was no difference in lifetimes over the concentration range 1×10^{-4} to 2×10^{-3} M within the error limit of 4%. The lifetime was also measured as a function of laser power and turned out to be independent of excitation intensity. The lifetimes of C_{60} and C_{70} in benzene solution were essentially identical with those in toluene solution. Our values of the lifetimes for S_1 states of C_{60} and C_{70} by the TCSPC technique confirm those of some of the earlier measurements by a less direct method of transient absorption, which reported lifetimes of 1.2 ns for C_{60}[8] and 0.67 ns for C_{70}.[10]

These results are in fact consistent with the weak fluorescence intensity observed (in our experiment), as first pointed out by Hochstrasser and co-workers.[9] If only the shoulder around 630 nm of the absorption spectrum is assigned to the $S_0 \rightarrow S_1$ transition, the radiative lifetime is estimated to be $2.9g_u$ μs, where g_u is the degeneracy of the emitting state, usually taken as 3. On the other hand, if the same transition gives rise to the entire visible absorption spectrum, a lower limit of the radiative lifetime is estimated to be $0.24g_u$ μs. Thus our measured excited-state lifetime of 1.17 ns for C_{60} yields the fluorescence quantum yield of $1.17\ \text{ns}/2.9g_u\ \mu\text{s} = 4 \times 10^{-4}/g_u$, with a possible upper limit of ca. $5 \times 10^{-3}/g_u$. Our previously estimated fluorescence quantum yield of ca. 2×10^{-4} not only is in good agreement with these results but also suggests that only a relatively narrow band of absorption is possibly due the $S_0 \rightarrow S_1$ transition.

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Supplementary Material Available: Mass spectra and mass spectral data for C_{60} and C_{70} (6 pages). Ordering information is given on any current masthead page.

Equivalent Li···O and H···O Electronic Effects in the Lithium Enolate of 1,3-Cyclohexanedione

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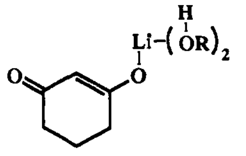
The question of the structural and electronic equivalence of lithium and hydrogen has been addressed both theoretically and experimentally.[1] The current view is that lithium structures are more complex than their H-bonded analogs due to the multiple coordination sites available for lithium. In addition, interactions between Li and electron-rich atoms like oxygen and nitrogen are stronger than the similar interactions involving H. We report here two unexpected structures containing both Li···O and H···O interactions where lithium and hydrogen have nearly identical coordinating abilities to the two conjugated oxygen atoms of 1,3-cyclohexanedione (CHD) lithium enolate (Li-CHD).



I. $R = -CH_3$

II. $R = -CH_2CF_3$

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[*] Alfred P. Sloan Fellow, 1989–1991.

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