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Electron transfer chemiluminescence of Buckminsterfullerene radical anion and thianthrene cation

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The electron transfer reaction between C_{60} (Buckminsterfullerene) radical anion and thianthrene radical cation has been carried out in methylene chloride for the first time, liberating an energy of 1.72 eV which is sufficient to form the first triplet state of C_{60} . This reaction produces a red chemiluminescence. The excited singlet state appears to be formed by a triplet-triplet annihilation reaction.

RECENTLY several authors¹⁻⁵ reported the fluorescence and phosphorescence properties of fullerenes, especially of C_{60} and C_{70} in condensed media. The fluorescence (at room temperature) and phosphorescence (only at 77 K) emissions were observed in the red spectral regions (600-800 nm). These studies have established that the first triplet and singlet states energies of C_{60} are located at $E_{T_1} = 1.56$ eV and $E_{S_1} = 2.00$ eV (refs. 1-3).

A question that stems from these studies is that whether it is possible to populate these excited states through chemical reactions involving fullerenes via electron transfer reactions of their radical ions. From a consideration of the above energies and Marcus theory of electron transfer reactions^{6,7} it is evident that if a chemical reaction between fullerene radical anion and a suitable radical cation can be initiated with a negative free energy change equivalent to or greater than E_{S_1} or E_{T_1} then it should be possible to produce the excited singlet state either directly or via triplet-triplet annihilation⁸⁻¹⁰. As it has so far not been feasible to produce a stable radical cation of fullerene (C_{60} or C_{70}) a reaction involving it with its own radical anion cannot be considered; stable radical anion of fullerenes has, however, been generated electrolytically in a number of studies¹¹⁻¹⁴. In the light of this limitation, one will have

to examine the electron transfer reactions with other stable radical cations which could be generated electrochemically. Thianthrene radical cation is a good choice for this purpose as it can be generated electrochemically and is stable for several minutes^{15,16}. So we report here the first case of an electron transfer reaction between fullerene radical anion and thianthrene radical cation to produce a chemiluminescence.

The experiments were conducted using pure C_{60} (99.5%) (Strem Chemicals, USA) or the carbon soot which contains a mixture of C_{60} and C_{70} (2-20% of C_{60}/C_{70}) extracted with CH_2Cl_2 (supplied by Strem Chemicals, USA).

The current-voltage curve of solution of ~ 1 mM Buckminsterfullerene (C_{60}) in CH_2Cl_2 (SDS Fine Chemicals Ltd., b.p. 40°C) containing 0.1 M tetra-*n*-butyl ammonium fluoborate ($TBABF_4$, South Western Analytical Chemicals Company Inc.) showed three successive one electron cathodic peaks at $E_{pc}^I = -0.45$ V, $E_{pc}^{II} = -0.88$ V and $E_{pc}^{III} = -1.25$ V vs. SCE. The significant characteristics of cyclic voltammetry, $E_p - E_{p/2}$, $E_{pa} - E_{pc}$ and i_{pa}/i_{pc} are suggestive of a stable reduction product. Upon sweeping the potential towards positive potentials, there was no anodic peak within the potential window of this solvent. With a mixture of C_{60} and thianthrene (Aldrich Chemical Co., m.p. 154-156°C) in the above medium, an anodic peak due to the oxidation of thianthrene is observed at $E_{pa}^I = +1.32$ V vs. SCE. At the negative potentials the thianthrene reduction could not be observed within the potential limits available in this medium. Experiments carried out with 1 mg of carbon soot ($C_{60} + C_{70}$), 10 mM thianthrene and 0.1 M TBA BF_4 in CH_2Cl_2 showed the cathodic and anodic peaks as shown in Figure 1. No appreciable shift in peak potentials were observed by the presence of C_{70} in the medium. Although the original recordings were done with a

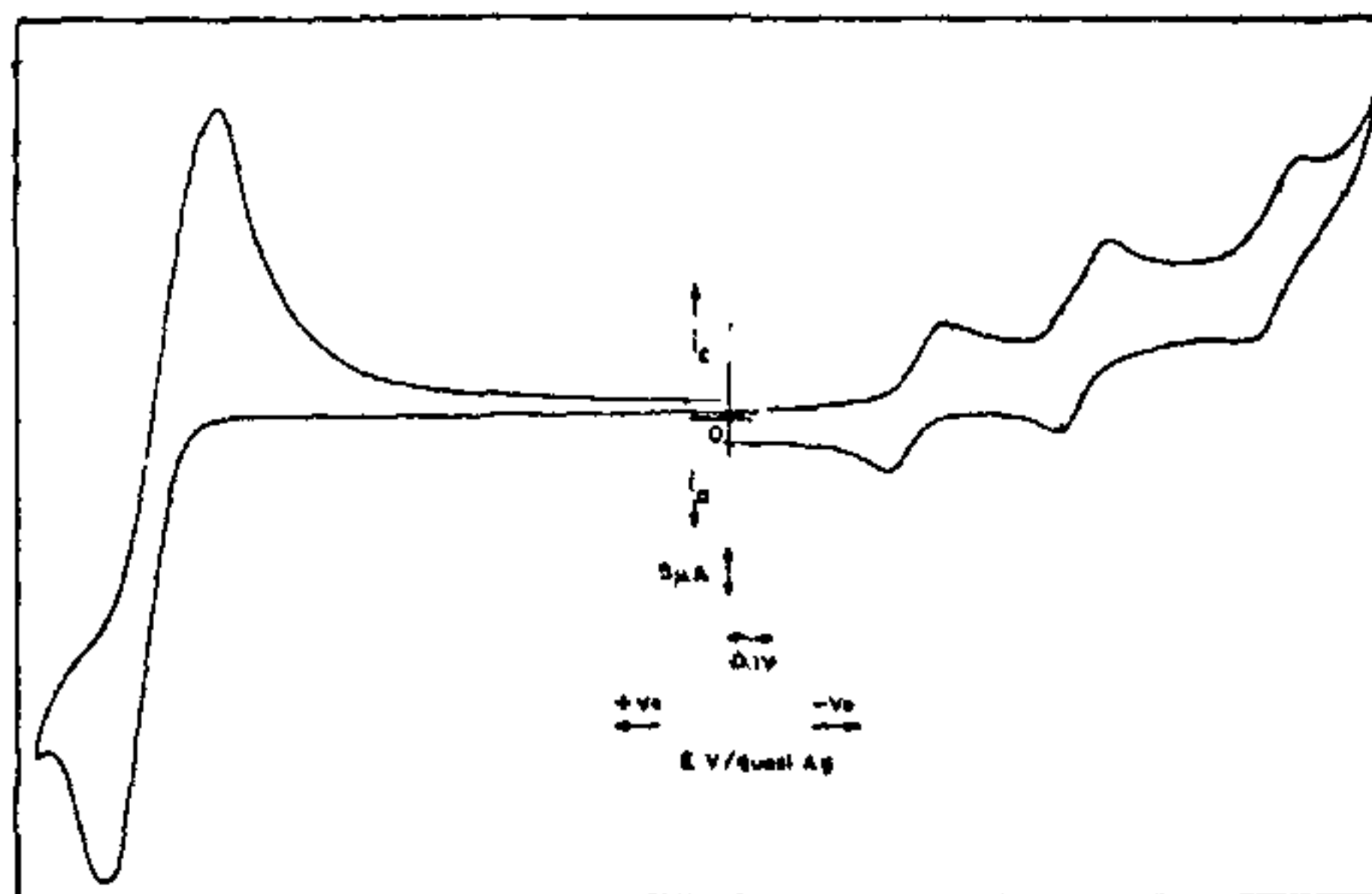


Figure 1. Cyclic voltammograms of the fullerene ($C_{60} + C_{70}$) and 10 mM thianthrene mixed system in methylene chloride containing 0.1 M TBA BF_4 . The area of the platinum wire electrode is 0.014 cm². Scan rate = 50 mV/s.

quasi Ag wire reference electrode to facilitate the use of a three electrode vacuum cell^{8,9}, the calibration of the reference electrode was carried out using 1 mM ferrocene as standard. This method prevented the contamination of the solution with water which would occur by using an aqueous saturated calomel electrode. The complementary anodic peaks are clearly seen in the figure. The cathodic and anodic peak currents increase with increasing sweep rate as expected for reversible electron transfer reactions¹⁷.

In order to examine the electron transfer reaction, the potential of the working electrode is stepped from 0 V to +1.40 V for a time of forward electrolysis of $t_f = 0.1$ s or 0.2 s or 0.5 s or 1 s or 2 s or 5 s. During this period the radical cation of thianthrene (red-coloured radical) is generated having a diffusion profile expected of Cottrell's equation¹⁸. At the end of this time the potential is stepped to a negative region of -0.45 V where radical anion of C_{60} is generated. In some experiments the potential programming was done to generate the dianion and trianion of C_{60} . As the free radicals of anion and cation exist in a region close to the electrode surface, a favourable electron transfer reaction can be examined by this method. The electrochemical cell is kept in a Turner luminometer which has the provision to integrate the photons liberated in the reaction and to simultaneously record the intensity decay profiles. With the above programming, the photon emission occurred at all the potential excursions; the number of photons emitted increased from fullerene mono-anion to trianion. The chemiluminescent efficiency is in the range of $\phi = 10^{-3} - 10^{-4}$. Upon cycling the potential of the working electrode between +1.40 V and -0.5 V for a $t_f = 0.5$ s and for a reversal electrolysis of the same duration, the chemiluminescence intensity decreased from its first cycle value to reach a steady state intensity as shown in Figure 2. This behaviour can be attributed to the diffusional limits imposed by the supply of the reactants and products. A similar chemiluminescent intensity decay behaviour has been observed for other t_f values. To examine the colour of this emission, different filters were introduced in front of the electrochemical cell and the intensities were monitored in the luminometer. The emission intensity is maximum in the red spectral region (600–800 nm). The control experiments have also been performed with no fullerene or thianthrene in the medium and also by having only fullerene or thianthrene in the medium. In either case there is no emission of light observed during the same potential limits.

On the basis of these preliminary data it is concluded that there is an efficient electron transfer reaction between thianthrene radical cation and fullerene free radical anion; the free energy released in this reaction is estimated at 1.72 eV using $-\Delta G = [E_{1/2}^{C_{60}^{\cdot-}/C_{60}} - E_{1,2}^{Th^{\cdot+}/Th}]$, where Th represents thianthrene. This suggests that a

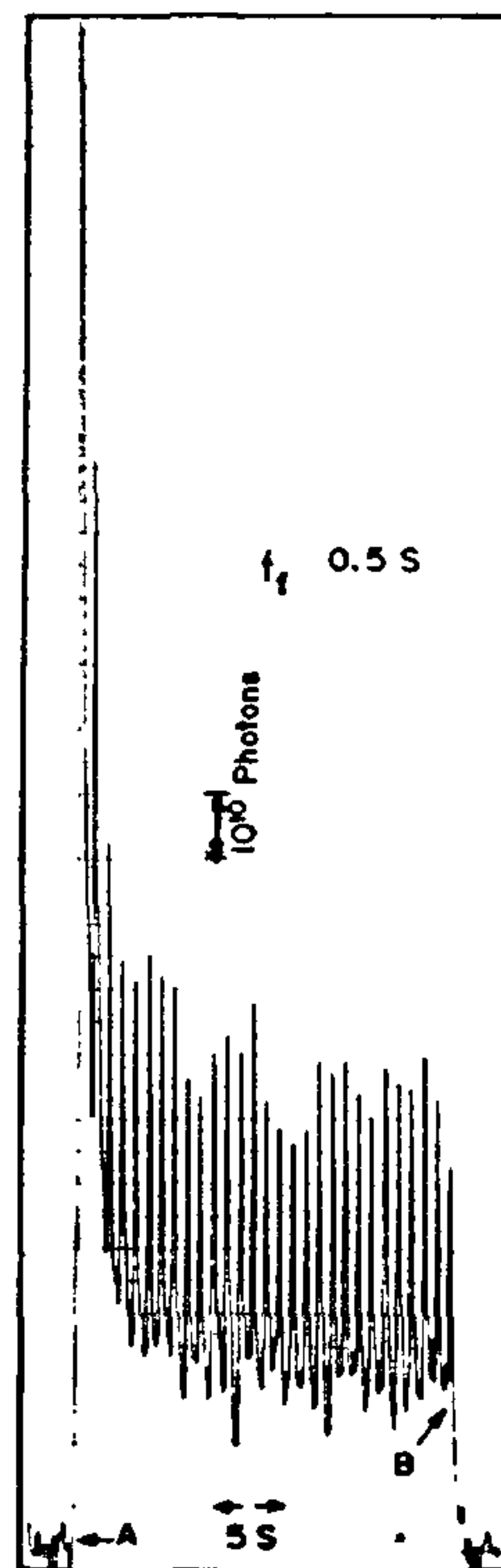
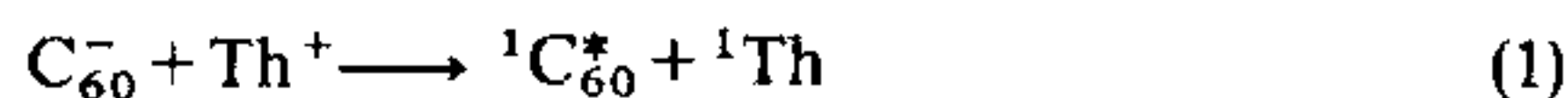
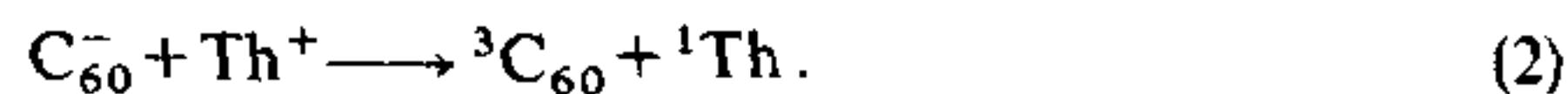


Figure 2. Chemiluminescence light intensity pulses in the repetitive pulse programming of potential of the working electrode from +1.4 V to -0.50 V for a $t_f = 0.5$ s. A and B refer to the application of the pulse and termination of the pulse. The recording is done through a luminometer. The solution contained fullerene ($C_{60} + C_{70}$), thianthrene and TBA BF_4 .

direct formation of the excited singlet state ($E_{S_1} = 2.0$ eV) of fullerene

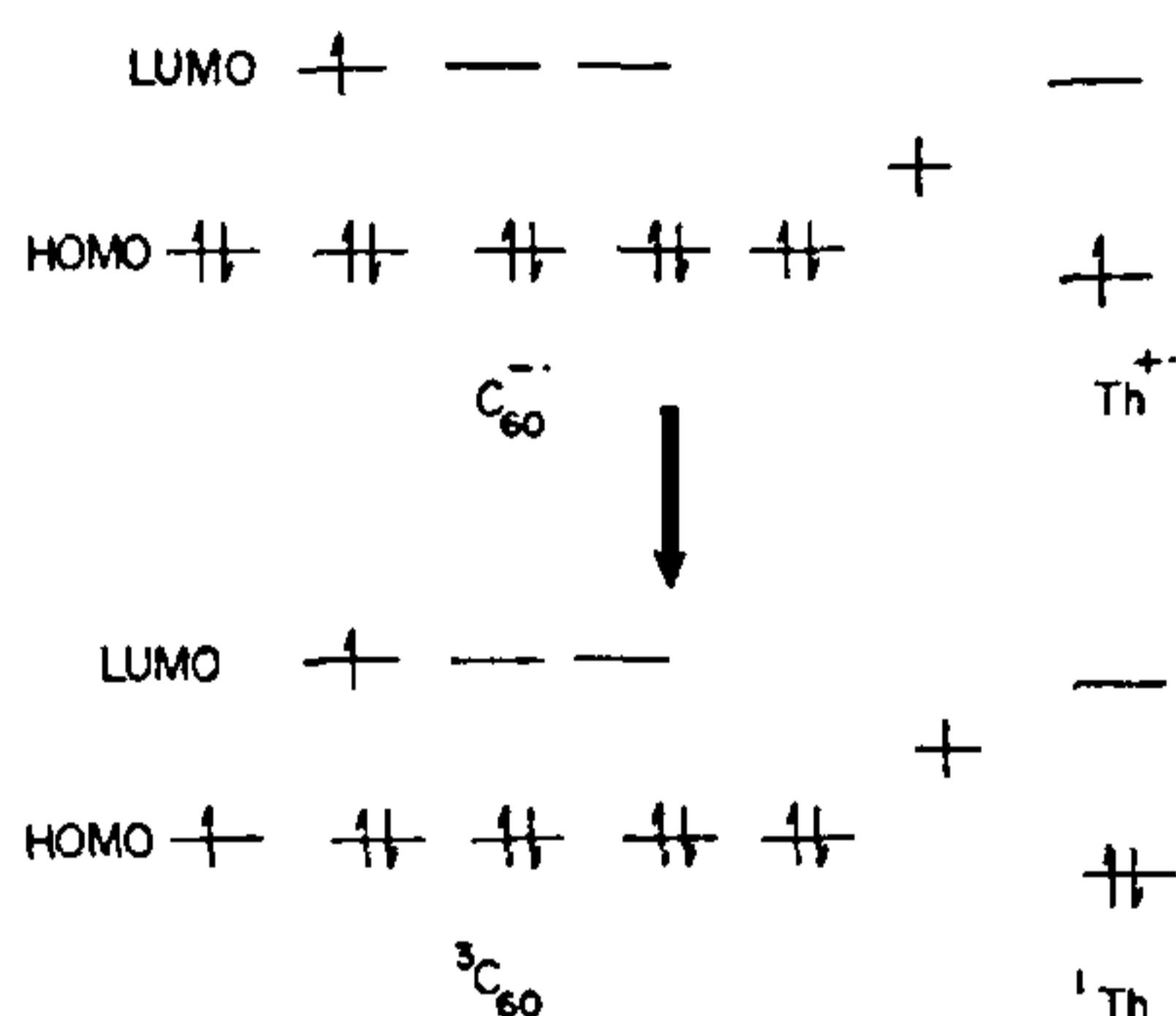


is thermodynamically hindered. As the triplet and singlet states of thianthrene are situated at $E_{T_1} = 2.62$ eV (ref. 19) and $E_{S_1} = 2.84$ eV (ref. 20) the formation of these states is also not feasible in the electron transfer reaction. Thus the electron transfer reaction can produce only the triplet state ($E_{T_1} = 1.56$ eV) of the fullerene through the following reaction scheme.



The triplets of C_{60} can annihilate via triplet-triplet

annihilation to produce C_{60} singlet state which subsequently can give a photon (chemiluminescence). There is a possibility of a heteroexcimer formation in these electron transfer reactions; however, we do not have yet any evidence for this process. Interestingly theoretical calculations have been performed on the distribution of the π electrons of C_{60} which show five highest occupied molecular orbitals (h_u) as degenerate and three lowest vacant unoccupied molecular orbital with symmetry t_{1u} (ref. 21). The free radical anion has been shown to have an odd electron in one of the three vacant molecular orbitals; this arrangement then suggests the electron transfer reaction between fullerene anion and thianthrene cation as taking place via the following scheme.



This is an interesting case of a triplet formation through the degenerate molecular orbitals*; in several other electron transfer reactions with aromatic hydrocarbons this degeneracy does not exist^{8,10}.

*After submitting this manuscript, we have carried out experiments on triplet state quenching by carrying out the electrolysis in the presence of O_2 . The emission intensity is quenched by the presence of O_2 . However, it should be noted here that O_2 could also affect the stability of the radical anion of C_{60} .

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Crystal structure of a tripeptide, glycyl-D, L-leucyl-L, D-alanine

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The crystal structure of a tripeptide, glycyl-D, L-leucyl-L, D-alanine has been determined by X-ray methods and refined to a final R -index of 0.079. There are two crystallographically independent molecules in a monoclinic unit cell with $a=17.817(2)$, $b=10.276(2)$, $c=18.451(3)\text{\AA}$, $\beta=116.95(3)$, $Z=8$ and space group $P2_1/n$. Both the molecules exist as zwitterions and adopt essentially similar conformation, with the backbone folding characteristic of a type II reverse turn. Even the leucyl side chains assume essentially similar conformation in the two independent molecules. The packing of the molecules involves spatial segregation of the leucyl side chains.

STRUCTURAL and conformational studies on oligopeptides are useful in theoretical modelling studies of protein folding from amino-acid sequence data. Moreover, since the conformation of even small peptides appears to be the major determinant of their functional properties under physiological conditions, structural studies on peptides in general should provide valuable information in the analysis of structure-activity relationships in biologically important peptides. As part of a series of structural studies on peptides¹, this paper describes the