Photochemical reaction between anthracene and carbon tetrachloride: Synthesis and isolation of 9-chloro-10, 10'-bis-(dichloromethylene)- (9'H)-10, 10'-dihydro-9, 9'-bianthryl (CDDB)

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Abstract. 9-Chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB) is the main bichromophoric photoproduct among the various such products obtained on photochemical reaction between anthracene and carbontetrachloride. This is confirmed by various analyses e.g. C–H–N analysis, IR, NMR and mass spectroscopy to establish its structure. In this ground state the dihedral angle between Cl–C₉–C_{9'} and C₉–C_{9'}–H is approximately 60°.

Keywords Photochemistry of anthracene; 9-chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB); bichromophoric molecule.

1. Introduction

When a solution of anthracene (A) in carbontetrachloride is irradiated with near-ultraviolet radiation from a high pressure Hg-discharge lamp, the solute reacts with the solvent with a quantum efficiency of 0.4. The process was explained by Bowen and Rohatgi (Rohatgi 1952; Bowen and Rohatgi 1953; Birk 1970; Rohatgi-Mukherjee 1988) as due to formation of $\cdot\text{ACl}$ + $\cdot\text{CCl}_3$ followed by further combinations of these radicals to give a number of products such as chlorinated anthracenes, anthracene dimers, substituted products of dihydro-anthracene etc. (Bowen and Rohatgi 1953; Selvarajan *et al* 1979) which may lose hydrogen chloride on standing or heating. They proposed an empirical structure as shown below of one of those photoproducts having the molecular formula $\text{C}_{30}\text{H}_{17}\text{Cl}_5$.

In this communication, we further show that the photoproduct is 9-chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB) which has been obtained in nearly 80% yield and characterised by C–H–N analysis, mass, IR and NMR spectroscopy.

2. Materials and experimental details

Anthracene (3g) (Koch-Light Lab) was dissolved in one litre of carbontetrachloride (E Merck, GR). This saturated solution of anthracene in some quartz reactors was deoxygenated by passing nitrogen gas for 30 min and then the reactor was sealed. These

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were then exposed to 366 nm radiation for 36 h from a Hg-discharge lamp. A golden-brown solution was formed, which was concentrated by distilling off the solvent under a filter pump. The concentrate was then dissolved in a small quantity of benzene and evaporated to dryness at low temperature. The residue was taken in cyclohexane solution and was subjected to chromatography on a column of active alumina. A number of bands were observed under UV light. The chromatography column was run using 3 litres of cyclohexane and the eluted volume was collected. The eluent was left undisturbed for evaporation. After some days it was observed that clusters of needle-shaped crystals were forming in the eluent. After complete evaporation, these clusters of light yellowish crystals were collected carefully leaving a dark tan coloured substance in the beaker. This was further purified by thin layer chromatography (TLC) on silica gel using benzene and chloroform (1:1) mixture. Two bands were seen: one at *r.f.* value 0.4 which was sharp and the other at *r.f.* value 0.7 which was not sharp and showed a mixture of substances. The latter layer was discarded. The layer with *r.f.* value 0.4 was collected and was dissolved in a benzene–chloroform mixture. Pure light yellow needle-shaped microcrystals were obtained. These microcrystals were further purified by TLC followed by recrystallization from cyclohexane. The compound was prepared three times and each and every time light yellow needle-shaped microcrystals were obtained. Though anthracene was of spectroscopic grade, it was purified by distillation in ethylene glycol as described in the literature (Vogel 1948). The solvents used were either spectroscopic grade (Fluka) or purified by standard methods as described in the literature (Vogel 1948) where GR quality solvents (E Merck) were used. The pure crystals have a sharp melting point at 105°C. The compound was further confirmed and established by (i) C–H–N, (ii) IR, (iii) NMR and (iv) mass spectral analyses.

2.1 C–H–N analysis

The C–H–N analysis of the solid gave C, 65.06%; H, 3.04% and no nitrogen; chlorine was tested by Piria and Sihiffs method (Clarke 1961) and gave Cl, 31.85%, compared to the theoretical values for $C_{30}H_{17}Cl_5$: C, 64.92; H, 3.06 and Cl, 31.94%. The analysis is in good agreement with the published data (Rohatgi 1952; Bowen and Rohatgi 1953).

2.2 IR spectrum analysis

IR spectrum was recorded on a Perkin–Elmer 597 IR spectrophotometer. The IR

Table 1. Assignments of IR vibrations.

Frequency (cm ⁻¹)	Tentative assignment
620(<i>s</i>)	C-Cl symmetric vibration
660(<i>s</i>)	C-Cl asymmetric vibration
700(<i>m</i>)	C-Cl stretching vibration (May be due to C-Cl vibrations at C ₉ position)
735 } 740 } (<i>vs</i>) 780 }	C-Cl stretching vibration (may be due to out-of-plane character)
1290 } 1310 } (<i>s</i>) 1340 }	C-H bending motion of alkene
1460(<i>s</i>) } 1490(<i>s</i>) } 1590(<i>w</i>) } 1600(<i>m</i>) }	Aromatic C=C bond stretching vibration
1640(<i>w</i>)	C=C stretching vibration in the middle rings of the two anthryl moieties
1685(<i>s</i>)	C=C stretching vibration (may be at C ₁₀ , C _{10'} position)
2970(<i>w</i>) } 3075(<i>w</i>) }	C-H stretching vibration (may be due to C-H vibration at C ₉ position)

Abbreviations: *s* = strong, *vs* = very strong, *m* = medium, *w* = weak.

spectral analysis shows the vibrations of different double and single bonds in-plane and out-of-plane. The major assignments are as in table 1 (Bellamy 1959; Dyer 1965).

2.3 NMR spectrum analysis

¹³C and ¹H NMR spectra were recorded on a BRUKER, FT-NMR, 500 MHz instrument. The spectral analysis of ¹H NMR in CDCl₃ is as follows: δ(300 MHz) 4.98(*s*, 1H), 7.37(*t*, 4H, 7.5 Hz), 7.49(*t*, 4H, 7.5 Hz), 7.68(*d*, 4H, 7.6 Hz), 7.89(*d*, 4H, 7.8 Hz).

The spectral analysis of ¹³C NMR in CDCl₃ is δ(75 MHz), 142.5(C=CCl₂), 132.6(C₁₀C_{10'}), 132.0, 128.7, 126.6, 125.3 (aromatic C-H carbons), 68.2(C₉), 29.6(C₉).

2.4 Mass spectral analysis

The mass spectra from different instruments at 70 eV showing the peak positions of the major fragments on the basis of *M/Z* values are shown in scheme 1. The number in the bracket indicates the relative intensity. Due to the presence of the chlorine atom in a CDDB molecule the molecular mass is to be counted taking two isotopes of chlorine e.g., ³⁵Cl and ³⁷Cl which exist in 3:1 ratio. The total number of peaks can be calculated from the binomial expansion of (*a* + *b*)^{*n*}, where *a* and *b* are the relative abundances of the isotopes and *n* the number of these atoms present in the ion (Kemp 1987). Thus for five chlorine in CDDB expansion gives *a*⁵ + 5*a*⁴*b* + 10*a*³*b*² + 10*a*²*b*³ + 5*ab*⁴ + *b*⁵. Six peaks should arise at 552, 554, 556, 558, 560, 562 and since the relative abundances of ³⁵Cl and ³⁷Cl are 3:1 (that is *a* = 3, *b* = 1) the intensities of the six peaks (ignoring contributions from other elements) are *a*⁵ = 243, 5*a*⁴*b* = 405, 10*a*³*b*² = 270, 10*a*²*b*³ = 90, 5*ab*⁴ = 15, *b*⁵ = 1 (that is in the ratio 243:405:270:90:15:1). The mass spectrum of

Scheme 1.

CDDDB shows four peaks at 552, 554, 556, 558 in the ratio 6:8:7:2. Due to weak intensities, the last two peaks at 560 and 562 have not been observed. In other fragmented ions the isotopic effect of chlorine is also pronounced but to keep the spectrum simple, the mass and relative intensity of the fragmented ions due to ^{35}Cl are only shown.

3. Discussion

The photochemical reaction between anthracene and carbontetrachloride gave mainly three substances (Rohatgi 1952; Bowen & Rohatgi 1953) viz. small amounts of 9-chloro and 9,10-dichloroanthracene and large amount of a solid having molecular formula $\text{C}_{30}\text{H}_{17}\text{Cl}_5$ (CDDDB). Gauche configurations (figure 3) of the molecule may be the ground state of the molecule which can be easily visualised using Newman projections of various molecular structures as shown in figures 1, 2 & 3.

When the dihedral angle between $\text{Cl}-\text{C}_9-\text{C}_8$ and $\text{C}_9-\text{C}_8-\text{H}$ planes in CDDDB is zero degree, the molecule is in 'totally eclipsed' configuration (figure 1), which makes the molecule highly unstable due to large energy arising out of the strong steric hindrance between the hydrogen atoms at C_1, C_1' and C_8, C_8' as well as Cl and H atoms at C_9 and C_9' respectively. Further rotation of the C_9-C_8 bond making the aforementioned dihedral angle 120° and 240° yields the two partially eclipsed conformations (not shown in figure) where strong steric hindrance exists due to H at C_9 and C_{9a} in the first

Figure 1. Structure of the compound in eclipsed form and its Newman projection.

Figure 2. The compound in staggered form and its Newman projection.

one and H at C_9 and C_{8a} in the second one. The 'staggered' conformation (figure 2) derived from rotation of the $\text{C}_9-\text{C}_9'$ bond by 180° is also energetically unstable due to strong steric interaction between hydrogens at C_1, C_8' and C_1', C_8 . Only in 'gauche' conformation where the dihedral angle is 60° and 300° , should the interaction be minimum due to the absence of appreciable steric hindrance between the atoms of the

Figure 3. The gauche form and the corresponding Newman projection.

two moieties. Therefore this 'gauche' conformation (figure 3) is the lowest energy state of the molecule.

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References

- Bellamy L J 1959 *The infrared spectra of complex molecules* (New York: John Wiley) 2nd edn
- Birk J B 1970 *Photophysics of aromatic molecules* (New York: Wiley Interscience) p. 439
- Bowen E J and Rohatgi K K 1953 *Faraday Soc. Discuss.* **14** 146
- Clarke H T 1961 *A hand book of organic analysis* (London: Orient Longmans) 4th edn p 308
- Dyer J R 1965 *Application of absorption spectroscopy of organic compounds* (Engelwood Cliffs: Prentice Hall) chap. 3
- Kemp W 1987 *Organic spectroscopy* 2nd edn (London: ELBS/Macmillan) chap. 5, p 231
- Rohatgi K K 1952 *The photochemical reaction of anthracene and allied substances*, D Phil thesis, Oxford, UK
- Rohatgi-Mukherjee K K 1988 *Fundamentals of photochemistry* (New Delhi: Wiley Eastern) chap. 11, p. 336 and references therein
- Selvarajan N, Panicker M M, Vaidyanathan S and Ramkrishnan V 1979 *Indian J. Chem.* **A18** 23
- Vogel A J 1948 *Practical organic chemistry* (London: Longmans) p. 826