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MOLECULAR STRUCTURE OF CYCLOADDUCT OF N-ETHOXYCARBONYLAZEPINE AND PHENCYCLONE: A STRUCTURE REVISION

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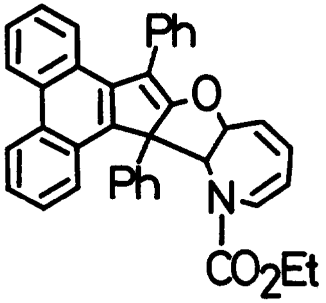
We reported previously that the cycloadduct from the reaction of phencyclone with N-ethoxycarbonylazepine was assigned as the [6+2]π adduct (I) in stead of expected [6+4]π or [4+2]π adduct based on chemical transformation.1) However, on mechanistic ground, there still leaves some ambiguity on the assignment. The present result led us to the conclusion that the structure of I should be revised to the [4+2]π adduct (II) by an X-ray crystallographic study.

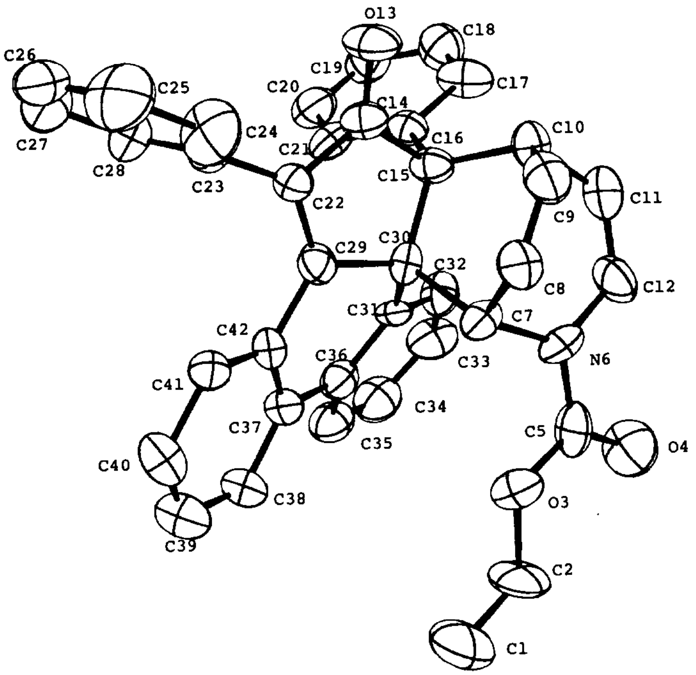
Single crystals of II were obtained from the ethanol-acetone solution by slow evaporation at room temperature. Unit cell dimensions were obtained from least squares refinement of the 2θ angles of 15 reflections measured on a Syntex $P\bar{1}$ automatic diffractometer (Mo, λ=0.71069 Å). The crystals are orthorhombic, space group $P2_1/n$, which is judged from systematic absence of reflections and there are four molecules in the unit cell of dimensions a=15.119, b=14.532, c=13.042 Å, β=91.40°. Intensity data were collected using the θ-2θ scan technique and of the 3923 independent reflections within the range of the diffractometer ($2\theta \leq 55°$), 1927 were observed. The structure was solved by the direct method using the MULTAN series of programme.2) E maps computed with the 467 normalized structure factors with values of $E \geq 1.5$ revealed the entire structure except hydrogen atoms. Refinements were carried out by the block-diagonal least-squares method using BDLS-60 programme.3) Final R value was 0.068 4) for the observed reflections.

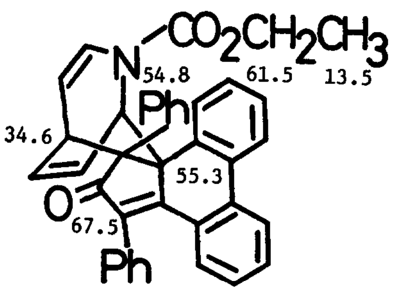
As can be seen in the computer generated drawing,5) II is endo[4+2]π cycloadduct from N-ethoxycarbonylazepine (4π) and phencyclone (2π). The bond lengths and the angles lie in the normal ranges. With this result in mind, we can consequently explain an unexpectedly low carbonyl absorption at 1700 cm^{-1} to be ascribable to two different carbonyl groups (-COCH=CH- and NCOOEt) which are overlapped each other. The UV spectrum of the adduct shows a enone chromophore (λ_{max} (hexane) 323 (log ε 3.92) and 352sh nm (log ε 3.75)) that matched that of II but not that of I. The six signals for sp^3-hybridized carbon at 13.5, 34.6, 54.8, 55.3, 61.5 and 67.5 ppm in ^{13}CMR spectrum are agreement with the assigned structure (II). In the reaction of phencyclone with various olefins, phencyclone behaves as a 4π-component showing the high peri- and regiospecificity.1) However, with phencyclone and N-ethoxycarbonylazepine phencyclone reacted as a 2π-component.

Although we cannot explain the anomaly at present stage, we are satisfied that the original report was in error. Other aspects of the regiochemistry of phencyclone are currently under investigation in our laboratory.



I





II

ORTEP drawing of II

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References

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2) G. Germain, P. Main, and E. W. Woolfson, Acta Cryst., B24, 274 (1970).
3) All the calculations were performed on the FACOM M-190 computer in the Computer Center of Kyushu University with the Universal Crystallographic Computation Program System UNICS II (Sakurai, Iwasaki, Kobayashi, Bando, and Nakamichi, 1974).
4) Thermal parameters of the hydrogen atoms were fixed so that B=3.0.
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