

Nature of the Interaction of Olefin–Bromine Complexes. Inference from (*E*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene, the First Example of an Olefin Whose Reaction with Bromine Stops at the Stage of π Complex Formation

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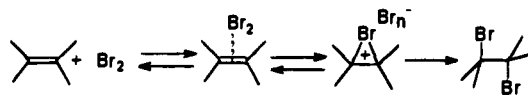
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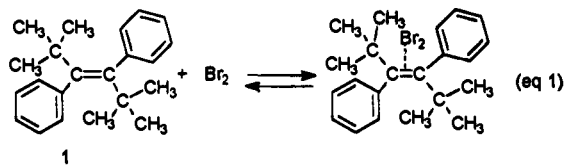
Olefin–bromine π complexes have been known for a long time to be the first species resulting from the interaction of the two reagents¹ and have been shown to be essential intermediates of olefin bromination,² being the direct precursors of the bromonium–bromide (or polybromide) ion pairs whose collapse leads to the final dibromide products (Scheme 1). Nevertheless, little experimental data exist for these π complexes, mainly because of their very high rate of ionization, which usually makes them detectable only by fast spectrokinetic methods, such as the “stopped-flow” technique.^{2,3} These methods, however, provide information only about the formation constants and electronic absorptions and not about the nature of these π complexes. Theoretical calculations⁴ indicate that charge transfer is almost negligible, and does not provide significant stabilization. Dispersion energy is the main driving force for binding.⁴ In agreement with this are the results obtained for ethylene–BrCl and ethylene–Cl₂ complexes with a new gas phase microwave spectroscopy technique,⁵ showing that the structural parameters of both olefin and halogen are not significantly changed on complexation and that the interaction of the π orbital with the halogen is weak.

(*E*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene (**1**) is a sterically congested stilbene which is not brominated but, in contrast to its inability to give a silver complex,⁶ forms a stable π complex with Br₂ at the olefinic double bond, which does not further react to a bromonium ion, and is therefore amenable to

Scheme 1



conventional UV–vis and NMR measurements in solution. These measurements allowed us for the first time to exclude a significant perturbation in the charge distribution of the complex.



The formation of a π complex between **1** and Br₂ (eq 1) was revealed by the appearance of a new UV-stable absorption band centered at 280 nm when the olefin and Br₂ were mixed in 1,2-dichloroethane. Such a band was not observed in solutions containing Br₂ and a large excess of toluene, showing that the site of complexation of **1** was not the phenyl ring but the olefinic double bond. The absorbance of the new band increased linearly when [1] was increased up to 1.5×10^{-1} M at constant [Br₂] = 2.3×10^{-3} M and when Br₂ was increased up to 2.5×10^{-2} M at constant [1] = 2×10^{-3} M, pointing to a 1:1 stoichiometry for the 1–Br₂ complex. All data obtained for solutions of 1.5×10^{-3} to 1.5×10^{-1} M olefin and 1.3×10^{-3} to 2.7×10^{-1} M Br₂ between 10 and 30 °C in the 270–370 nm wavelength range, where both the formation of the complex and the disappearance of Br₂ were observed, as well as at 450 nm, where only Br₂ disappearance was monitored, were simultaneously fitted using a previously described nonlinear least-squares procedure (NLLSQ).^{3a,7} Values of $\Delta H = -3.25(0.13)$ kcal mol⁻¹ and $\Delta S = -10.6(0.5)$ eu were obtained, corresponding to $K_f = 1.2(0.1)$ M⁻¹ at 25 °C. The maximum molar extinction coefficient was $\epsilon_{\max} = 5.6(0.5) \times 10^3$ M⁻¹ cm⁻¹ at $\lambda_{\max} = 280$ nm. The root mean square (rms) of the residuals of the fit was 0.034 abs units. The highest correlation coefficient, r , between the thermodynamic parameters and the molar extinction coefficients was reassuringly as low as 0.247.

The quality of this fit confirmed the 1:1 stoichiometry of the complex and excluded the formation of a bromonium–Br₃⁻ species of 1:2 stoichiometry. An equilibrium between olefin–Br₂ complexes and bromonium polybromide salts had been found in solutions of adamantylideneadamantane and Br₂.⁸ Thus, (*E*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene is the first reported example of an olefin whose interaction with bromine is limited to π complex formation.⁹

A comparison of the obtained thermodynamic parameters with those reported^{3c} for the 1:1 complex of (*E*)-2,2,3,4,5,5-hexamethylhex-3-ene with Br₂ shows that the substitution of two methyls with two unconjugated phenyl groups¹⁰ at the double bond results in a *ca.* 70-fold decrease in K_f and a 2.5 kcal mol⁻¹ decrease in the absolute value of ΔH , probably due to the larger steric requirements of **1**.

The ¹H and ¹³C NMR spectra of **1** (0.1 M) in dichloromethane-*d*₂ at –35 °C showed respectively a singlet at δ 0.68

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(9) An earlier observation of unreactivity toward Br₂ was made by Olah for tetraeneopentylethylene (Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580). No π complex was claimed to be formed between these two reagents on the basis of the ¹³C NMR spectrum, which, however, we are showing not to be diagnostic. An accurate re-examination of this system is presently in progress in these laboratories.

(10) The UV spectrum of **1** was more like that of toluene than those of stilbenes: Gano, J. E.; Park, B.-S.; Subramaniam, G.; Lenoir, D.; Gleiter, R. *J. Org. Chem.* **1991**, *56*, 4806.

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(7) The K_f of the complex could not be obtained by Benesi–Hildebrand type equations (Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167) using data obtained at a single wavelength because of the too high correlation of K_f and ϵ .

Table 1. ^1H and ^{13}C NMR Chemical Shifts (ppm) Calculated by the IGLO Method

	ethylene	ethylene in π complex geometry	π complex
C	131.48	133.04	133.21
H	6.51	6.60	6.79

and an aromatic multiplet at δ 7.22, 7.24, 7.245, 7.265, 7.28, 7.30, 7.305, 7.325, and 7.34 ppm and *tert*-butyl carbon signals at 32.38 (CH_3) and 37.31 ($>\text{C}<$), aromatic carbon signals at 125.62, 126.46, and 130.59, and quaternary aromatic and olefinic carbon signals at 143.70 and 144.75 ppm. Both the ^1H and the ^{13}C spectra remained absolutely unchanged after addition of a 2-fold molar excess of Br_2 . Under these conditions and on the basis of the thermodynamic parameters determined in the very similar 1,2-dichloroethane solvent, about one-half of the olefin was present as a complex with Br_2 . These spectra showed no change during several hours, confirming that the π complex did not react further to a bromonium species, for which large downfield shifts in both the ^1H and the ^{13}C NMR signals were expected.^{11,12}

In order to explain the observed fact that adding bromine to the solution of the title olefin in dichloromethane- d_2 does not lead to any observable change in the ^{13}C NMR spectrum, we performed ab initio energy and chemical shift calculations on the parent model system ethylene + Br_2 .

The geometries of ethylene, bromine, and the π complex of ethylene with bromine were optimized at the MP2/6-31G* level of ab initio theory using an Ahlrichs SVB basis for bromine.¹³ The heat of complex formation was found to be exothermic by 3.1 kcal/mol (including ZPE). Our results confirm the T-shaped C_{2v} structure of the complex found earlier.⁴ The distance between bromine and the π plane is 2.92 Å.¹⁴ In agreement with calculations of Kochanski et al.,⁴ the charge that is transferred during complex formation is rather low (0.06 electrons). IGLO chemical shift calculations¹⁵ were performed using ab initio calculated geometries. The results are summarized in Table 1. To exclude basis set superposition errors we used the counterpoise method¹⁶ within the IGLO calculations.

The calculation indicates that a 1.7 ppm downfield shift as a result of complex formation should be observed. However, the change in chemical shift is due almost exclusively to the

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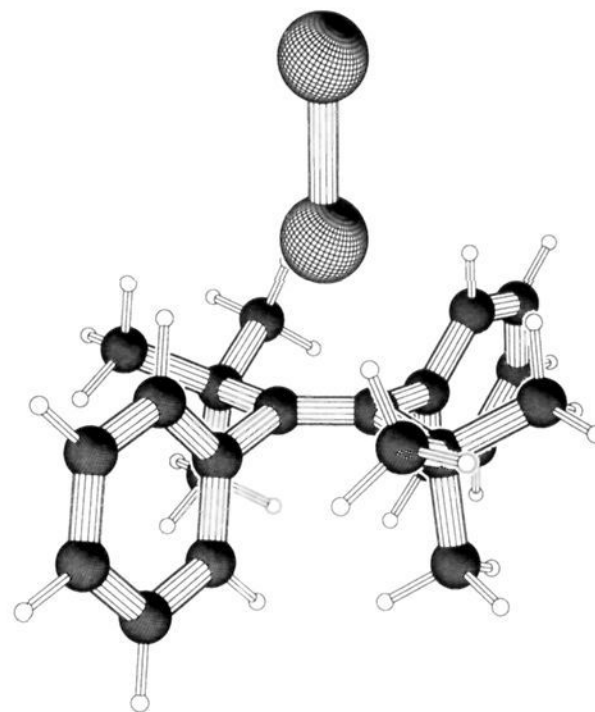
(12) The bromonium ion formation produces a downfield shift of 23 ppm in the olefinic carbons of adamantylideneadamantane in dichloromethane- d_2 .

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(14) A recent ab initio calculation of the ethylene- Br_2 system has also shown the formation of a 1:1 ethylene- Br_2 complex. The distance of bromine from the π plane is, however, higher (3.523 Å) than that found in the present calculation (Cossi, M.; Persico, M.; Tomasi, J. *J. Am. Chem. Soc.* **1994**, *116*, 5373).

(15) IGLO (individual gauge for localized orbitals); for a review, see: Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR* **1990**, *23*, 165.

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**Figure 1.** PM3 energy-minimized conformation of the (*E*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene- Br_2 π complex.

geometry change that is induced by steric effects of the bromine (see “ethylene in π complex geometry”, Table 1). Charge transfer, which is very weak (see above), accounts for only 0.17 of the total change of 1.7 ppm. Thus it can be concluded that in the sterically extremely congested title olefin only a very small change in chemical shifts is to be observed on π complex formation, which is in agreement with our observations.

Further information about the reasons why the bromination stops at the π complex stage was given by a PM3 calculation of the **1**- Br_2 complex. Both phenyl rings are perpendicular to the π plane of the double bond, and the ortho hydrogen atoms, together with the *tert*-butyl groups, prevent a further approach of bromine (Figure 1).

In conclusion, the results of the present investigation provide the first experimental evidence, corroborated by theoretical calculations, that the olefin-bromine complexes formed as the first products of the interaction of the two reagents are actually of the Mulliken “outer” type.

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Supporting Information Available: Multifrequency, multitemperature fitting of the absorbances against the analytical olefin and Br_2 concentrations, giving ΔH and ΔS for π -complex formation and its molar extinction coefficient at each examined wavelength, the rms, and the correlation coefficients r between the molar extinction coefficients and the thermodynamic parameters at each wavelength, and table of the employed analytical concentrations of Br_2 and **1** showing the calculated equilibrium concentrations of free Br_2 , free olefin, and olefin- Br_2 π complex (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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