The TCNE-Benzene Complex: A CNDO Approach*

D. B. Chesnut and Paul E. S. Wormer**

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received October 9, 1970

CNDO/2 calculations on the TCNE-benzene complex are reported. A stable complex is found which exhibits a relatively large stabilization energy (0.2 a.u.) at a short interplanar separation (1.75 Å); the binding apparently arises solely through charge transfer. Mulliken population analyses were performed by reinterpreting the CNDO orbitals as Löwdin orbitals. Sample calculations on small organic molecules and first row diatomics indicate the procedure to be satisfactory. It is shown that generally only overlap populations that are summed over the orbitals of the atoms in question reflect the symmetry of the molecule.

Die Ergebnisse von CNDO/2-Rechnungen an Tetracyanoäthyl-Benzol-Komplexen werden mitgeteilt. Es wird ein stabiler Komplex gefunden, der eine relativ große Stabilisierungsentnergie (0.2 A.E.) bei geringem Abstand (1.75 Å) der Molekülebenen besitzt; die Bindung entsteht anscheinend nur durch Ladungsübertragung. Eine Populationsanalyse nach Mulliken wurde mit Hilfe der Interpretation der CNDO-Orbitale als Löwdin-Orbitale durchgeführt. Berechnungen an Beispielen wie kleinen organischen Molekülen und zweiatomigen Molekülen aus Elementen der ersten Reihe zeigen, daß die Methode befriedigende Ergebnisse liefert. Es wird gezeigt, daß im allgemeinen nur die Überlappungs-Populationen, die über die Orbitale der betrachteten Atome summiert werden, die Symmetrie des Moleküls widerspiegeln.

Calculs CNDO/2 sur le complexe TCNE-benzène. Un complexe stable apparaît pour une séparation interplan courte (1,75 Å) avec une énergie de stabilisation relativement forte (0.2 u.a.); la liaison provient apparemment du seul transfert de charge. Une analyse de population de Mulliken a été effectuée en réinterprétant les orbitales CNDO comme orbitales de Löwdin. Des calculs échantillonnés sur de petites molécules organiques et des molécules diatomiques de la première ligne montrent que le procédé s’avère satisfaisant. On montre qu’en général, seules les populations de recouvrement sommées sur les orbitales des atomes en question reflètent la symétrie de la molécule.

Introduction

π-π molecular complexes pose an interesting study in bonding. The question of the prime effect in stabilizing such systems is not yet clear due mainly to the difficulty in adequately treating such large systems. For some time it was generally felt that charge transfer stabilization was mainly responsible for bonding, but spectroscopic measurements on some TCNE (tetracyanoethylene) complexes do not seem to support this idea [1]. Studies employing a π-only extended Hückel approach [2] have given indications of reproducing relative molecular geometries at chosen experimental interplanar intermolecular separations but in general fail to predict absolute binding. The advent of approximate self-consistent field

---

* Supported in part by NASA University Sustaining Grant NGR 34-001-005 and National Science Foundation Grant GP-8298.

** Present address: Department of Theoretical Chemistry, University of Nijmegen, The Netherlands.
treatments introduced by Pople and coworkers [3] allows a more readily justifiable treatment of large systems and avoids many of the pitfalls of one-electron methods. For example, several recent calculations [4, 5] using this method on hydrogen bonded systems have yielded reasonable results. In the present paper we present CNDO/2 calculations of the TCNE-benzene complex for a restricted region of relative intermolecular geometry.

A basic purpose for initiating such a calculation is the elucidation of those factors which dictate the observed relative intermolecular geometry characteristic of the majority of both charge transfer and charge resonance complexes. Unfortunately, the current calculations do not reveal any particular simplifying feature; on the contrary, the issue is clouded a bit by our results which indicate small and negative intermolecular overlap populations and a high degree of charge transfer. It is worthwhile to discuss these results in light of the general problems above. Too, since no previous CNDO calculations on systems of this kind have been performed the present calculations may be taken as a model study of the CNDO approach to a π-bonded bimolecular system.

**Choice of Model**

The dominant structural fragment seen in most π-π molecular complexes consists of a bonds-over-bonds arrangement shown below,

![Diagram](attachment:diagram.png)

where the benzenoid moiety projects onto an ethylene-like fragment arising either from a real ethylene group (case a, as, for example, the central portion of TCNE itself) or from a fused benzenoid system (case b). Examples of such structures can be seen in Chesnut and Moseley’s paper [2] and from the review paper of Prout and Wright [6]. We wished to carry out calculations on a system that exhibits such a characteristic projected structure and at the same time was small enough to minimize computer time. The available program is limited to 80 orbitals which severely restricts our selection. The TCNE-benzene system represents a 70-orbital problem and, although its structure is not known, one would expect a behavior similar to the general class of materials. Indeed, the TCNE-naphthalene crystal structure is known [7], exhibiting the projection

![Diagram](attachment:diagram.png)