A Combination of Empirical Force Field and Extended Hückel Molecular Orbital Calculations as a Computational Approach to Conformational Analysis

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Abstract: A combined empirical force field (EFF)–extended Hückel molecular orbital (EHMO) approach to conformational analysis has been developed. This hybrid approach involves a full relaxation EFF calculation of conformer structures, followed by a single EH calculation on each structure. The new method appears to represent a useful adjunct to existing EFF calculations, especially in application to relative conformer energies of arene derivatives. Constitutional isomerism cannot be handled by the EFF–EHMO approach. Our results indicate that, contrary to previous notions, the EHMO method tends to underestimate conventional steric effects.

The empirical force field (EFF) method (molecular mechanics) has developed into a valuable source of data on structures and energies for hydrocarbons and other organic compounds.[1-3] The method is especially useful for studies of larger molecules to which molecular orbital (MO) calculations of either the ab initio or approximate types are inapplicable. Nevertheless, the reliability of the EFF approach is generally acknowledged to be greater in the prediction of structural parameters than of energies.[1] This conclusion is based on the observation that for a given molecule, different EFF parametrizations often yield nearly identical structures, but substantially different relative energies. Furthermore, several cases are known in which the EFF method leads to incorrect predictions of relative conformer energies (see below).

Tempting as it might be to correct each deficiency by choosing a new set of "readjusted" force field parameters designed to produce the proper results, such an approach almost inevitably leads to a continuing process of reparametrization, and thus to a proliferation of "improved" EFFs. An alternative, and inherently more appealing, solution to this problem utilizes an EFF for structure calculation and an MO method to compute relative energies. Indeed, several workers have taken this approach by coupling EFF and ab initio MO calculations.[4] Unfortunately, the cost of ab initio calculations is prohibitive for molecules of modest size. We were therefore led to investigate a combination of the EFF method with a much simpler (and far less expensive) MO approach: extended Hückel theory (EHT).[5] The cost of EH computations is trivial for even the largest molecules which can be handled by the EFF approach. Furthermore, the simplicity of this MO method is appropriately matched to the empirical nature of molecular mechanics.

The hybrid EFF–EHMO method involves a full relaxation EFF calculation of conformer (or, in general, isomer) structures, followed by a single EH calculation on each structure to determine relative energies.[6] We found (see below) that this method can be quite useful in predicting relative conformer energies, especially for arene derivatives. However, the EFF–EHMO method is not applicable to constitutional isomerism, and treats strain energies in only a qualitative way.

It must be emphasized from the start that there is no theoretical justification for the new hybrid method. What we present here is simply an inexpensive, *empirical* tool for the conformational analysis of relatively large molecules. At the same time, EFF–EHMO calculations allow a more reasonable evaluation of the intrinsic properties of EHT, in that geometries of essentially experimental quality are used, rather than standard geometries.

Although it is undeniable that the method contains an element of inconsistency, in the sense that EHT is being used to evaluate geometries which are not energy minima in EH space, it should be noted that this is almost always the case with EH calculations, since standard geometries are used. However, we believe that the results presented here demonstrate that EFF–EHMO can serve as a useful adjunct to the EFF method, especially in cases where straightforward EFF results are ambiguous (i.e., where energy differences are small).

Determination of Relative Conformer Energies

Arene Derivatives. Some years ago we developed an EFF for arene derivatives[8] based on Allinger's aliphatic field,[9] with the aromatic parameters of Boyd[10] scaled to match Allinger's. The remarkable success of this EFF in predicting structures and relative conformer energies[3] was marred by a notable exception:[11] our EFF failed to predict the correct ordering of conformer energies for bibenzyl (**1**) and 1,2-diphenylpropane (**2**). The energies separating the various conformers of these two compounds are rather small (Table I), and, since we were confident that our EFF had produced accurate geometries for these simple molecules, the most likely source of the problem seemed to be in the energy calculations. This case appeared to be a good one for a test of the EFF–EHMO approach. Application of the new hybrid method to these two compounds did indeed reverse the conclusions of the straightforward EFF approach and yielded an ordering of energies which was in excellent agreement with experiment (Table I).[12]

Another interesting case in which EFF results seemed to be at odds with experiment involved the conformational analysis of tetraphenylmethane (**3**) and tetraphenylsilane (**4**). In a previous study[15] of these systems by the EFF method,[8] two stable conformers (S_4 and D_{2d})[16] of roughly equal energy had been found for **4**, whereas a ground state with D_{2d} symmetry[16] was found for **3**. No energy minimum could be detected[15] for S_4-**3** even though X-ray diffraction results indicated that **3**,[17] as well as **4**,[18] possesses S_4 symmetry in the crystal.

Figure 1 summarizes the results of our EFF–EHMO calculations on **3** and **4**.[19] In agreement with previous EFF calculations[15] and with experimental findings,[18] **4** is predicted to have a stable S_4 form with $|\phi|$ ca. 40°, but the D_{2d} conformation is now found to correspond to an energy *maximum*. More startling is the finding of *two* energy minima on the conformational hypersurface of **3**. One of these has D_{2d} symmetry[16] and corresponds to the ground state of the molecule, in agreement with the previous EFF calculation.[15] The other conformer has S_4 symmetry, with $|\phi|$ ca. 50°, in excellent agreement with the X-ray value[17] of 48°, and lies 0.4 kcal/mol above the ground state. The preference of **3** for S_4 symmetry

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Table I. Conformer Energy Differences[a]

compd	conformer	EFF E_{rel}	EFF-EHMO E, eV	EFF-EHMO E_{rel}	exptl
bibenzyl (**1**)	anti	1.15[b]	−1236.7982	0	exclusively[c] or predominantly[d] anti
	gauche	0	−1236.7543	1.01	
1,2-diphenylpropane (**2**)	phenyls anti	1.26[b]	−1342.5754	0	0[e]
	phenyls gauche and methyl anti	0	−1342.5449	0.70	0.24
	phenyls gauche and methyl gauche	0.79	−1342.4826	2.14	0.83
tetraphenylethane (**5**)	anti	0[f]	−2225.1934	0	anti[f]
	gauche	4.96	−2224.9726	5.09	
bifluorenyl (**6**)	anti	6.55[g]	−2151.8462	10.72	gauche[h]
	gauche	0	−2152.3113	0	
hexaphenylethane (**7**)	D_3	0[g]	−3211.6841	0	
	S_6	2.55	−3211.4438	5.44	
pentaphenylethane (**8**)	**a**	0	−2718.6283	1.09	
	b	3.84	−2718.6756	0	**b**[i]
	c	0.26	−2718.5949	1.86	
n-butane (**9**)	anti	0 (0)	−459.8034 (−459.6904)	0 (0.18)	0[j]
	gauche	0.70 (0.93)	−459.7902 (−459.6983)	0.30 (0)	0.9
methylcyclohexane (**10**)	axial	1.68 (1.83)	−740.8644 (−740.8543)	0.057 (0)	1.8[j]
	equatorial	0 (0)	−740.8668 (−740.8478)	0 (0.15)	0
decalin (**11**)	cis	2.67 (2.7)	−1021.9181 (−1022.0004)	0.20 (0)	2.7[k]
	trans	0 (0)	−1021.9267 (−1021.9902)	0 (0.24)	0
cyclodecane (**12**)	BCB	1.68 (0.73)	−1058.1072 (−1057.9290)	0 (0)	BCB[l]
	TCCC	0 (0)	−1057.8767 (−1057.7179)	4.84 (4.87)	

[a] Values for relative conformer energies (E_{rel}) are in kcal/mol. Values in parentheses were obtained using the EAS force field,[29] others used ALL 71[9] for alkanes, and the EFF of ref 8 for arene derivatives. [b] Reference 11. [c] C. J. Brown, *Acta Crystallogr.*, **8**, 97 (1954); M. S. Mathur and G. C. Tabisz, *J. Cryst. Mol. Struct.*, **4**, 23 (1973). [d] K. K. Chiu, H. H. Huang, and L. H. L. Chia, *J. Chem. Soc., Perkin Trans. 2*, 286 (1972); A. M. North, R. A. Pethrick, and A. D. Wilson, *Spectrochim. Acta, Part A*, **30**, 1317 (1974). [e] Relative energies (kcal/mol) calculated from ref 11 and S. L. Spassov, A. S. Orahovats, S. M. Mishev, and J. Schraml, *Tetrahedron*, **30**, 365 (1974). [f] Reference 20. [g] Reference 22. [h] Reference 21. [i] Reference 23. [j] E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962. [k] Reference 29. [l] Reference 1.

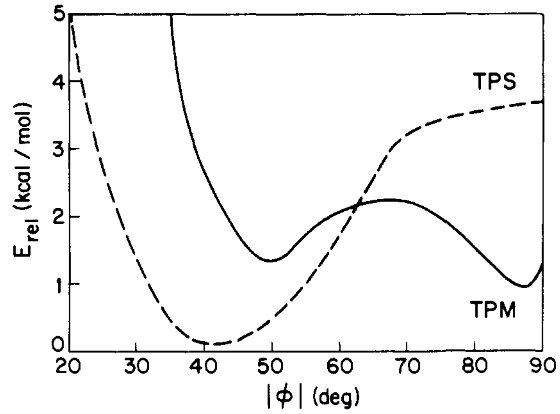

Figure 1. Relative EFF-EHMO energy as a function of the absolute value of the ring dihedral angle ($|\phi|$) for tetraphenylmethane (TPM, **3**, solid line) and tetraphenylsilane (TPS, **4** dashed line). The positioning of each curve on the energy scale is arbitrary.[19]

in the crystal is thus easily accounted for by invoking crystal packing forces, a suggestion previously advanced[15] on a more tenuous basis. Thus, in its application to **3**, the EFF-EHMO approach did more than merely reverse an incorrect EFF energy ordering: it also uncovered an energy minimum not previously located by straightforward EFF calculations.

Although the above results were highly encouraging, it remained to demonstrate that they were not simply manifestations of a general tendency of the EFF-EHMO method to reverse EFF results. Accordingly, we tested the new method on two structures for which EFF calculations are known to give correct predictions, 1,1,2,2-tetraphenylethane (**5**, anti)[20] and 9,9′-bifluorenyl (**6**, gauche).[21] In both cases, the hybrid method selected the correct ground state (Table I). The prediction by this method that the D_3 form of hexaphenylethane (**7**) is more stable than the S_6 form (Table I) is also in agreement with previous EFF calculations,[22] although in this case, of course, no experimental comparison is possible. This structure is the largest for which we have performed EH calculations. It contains 182 valence orbitals, but an EH calculation required only 85 s of CPU time on an IBM 360/91 computer.

A further application of the new method concerns the structure of pentaphenylethane (**8**). Simonetta and co-workers recently determined the crystal structure of a THF solvate of this compound by X-ray diffraction,[23] and compared their results with a structure (**8a**) calculated by our EFF[22] (Figure 2). The primary conformational feature of the molecule, i.e., the nonhelical nature of the phenyl ring twists, was correctly predicted by the EFF.[22,24] However, the calculated magnitudes of the ring twists (ϕ_r) and central ethane dihedral angles (ϕ_c) differ somewhat from those of the X-ray structure.[25] An EFF structure with all ring and central dihedral angles fixed at the X-ray values, but with all other parameters relaxed (**8b**), was calculated (EFF) to be 3.6 kcal/mol less stable than **8a**. Full relaxation of this structure gave a new EFF minimum (**8c**)

Table II. Relative Energies for Constitutional Isomers[a]

compd	EFF-EHMO		EHT[b]	exptl[c]
	ALL 71	EAS		
n-butane	0	0	2.3	1.63
isobutane	1.50	3.55	0	0
n-pentane	0	0	5.39	4.07
isopentane	2.12	1.32	9.24	2.49
neopentane	4.40	3.93	0	0
isobutylene	1.10	*d*	0	0
trans-2-butene	0		1.68	1.26
cis-2-butene	6.50		5.03	2.50
1-butene	3.63		5.54	3.98

[a] Values in kcal/mol. [b] Reference 5a. [c] Obtained from ΔH_f at 0 K, as listed in ref 5a. [d] The EAS EFF is not parametrized for olefins.

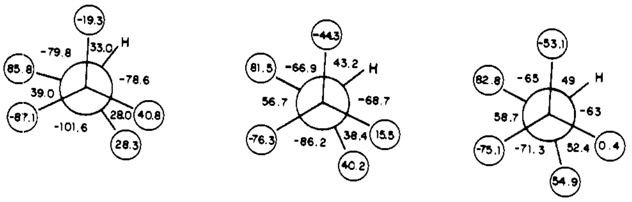

Figure 2. Calculated (EFF) structures of pentaphenylethane (**8**) showing ϕ_r's (in circles) and ϕ_c's: left, **8a**; middle, **8c**; right, **8b**.

which closely resembled the X-ray structure (Figure 2), and which was only 0.26 kcal/mol less stable than **8a**.[26] This finding illustrates an inherent difficulty in calculating the structures of large, asymmetric molecules by the force field method: the potential energy hyperspaces for such molecules are no doubt extremely complex, and one can never be certain that all the minima, inculding the global minimum, have been found.[27]

The EFF-EHMO results for **8** (Table I) are somewhat surprising. In accord with the EFF results, the hybrid method places **8a** slightly lower in energy than **8c**. However, the EFF-EHMO method finds the lowest energy structure to be **8b**. This structure corresponds most closely to the X-ray structure, but is not a minimum on the EFF hypersurface.

Aliphatic Compounds. Encouraged by our results for the arene derivatives, we next applied the EFF-EHMO method to several aliphatic systems. Unlike the aryl systems, the aliphatic compounds can be studied using a wide variety of EFFs. We chose to concentrate on the Allinger 1971 (ALL 71) EFF,[9] since this is the basis of our aryl force field. Generally, comparison calculations using the Engler-Andose-Schleyer (EAS)[29] force field were also performed.

We first studied three classical conformational effects: the gauche-anti difference in *n*-butane (**9**), the axial-equatorial difference in methylcyclohexane (**10**), and the cis-trans difference in decalin (**11**).[30,31] Appropriate relative conformer energies for **9-11** had been determined by Hoffmann in his original study[5a] of the EH method using standard geometries. In each case, EHT selected the correct conformer, but overestimated the energy difference by almost an order of magnitude. Results of this kind led to the conclusion that EHT overestimates "steric effects".[5a] Our EFF-EHMO results for **9-11** (Table I) reverse this finding. Using ALL 71, the EFF-EHMO method correctly predicts the ground-state conformer in each case. However, the hybrid method grossly underestimates the energy separation, again by roughly an order of magnitude. The calculated separation for **10** is especially disturbing. Using the EAS force field, the hybrid method consistently chooses the wrong conformational ground state for **9-11**, with energy differences again being quite small. The important conclusion is that EFF-EHMO results are evidently force field dependent.

Although our results for these small aliphatic systems are rather discouraging, the EFF-EHMO method has performed quite satisfactorily in a variety of applications to larger aliphatic systems. A well-known problem molecule for EFF calculations is cyclodecane (**12**). Both the ALL 71 and the EAS force fields choose a twisted chair-chair-chair (TCCC) conformer as the ground state,[29] while a variety of X-ray structures of simple derivatives of **12**, and some other EFFs[1] favor a boat-chair-boat (BCB) conformation. Although more recently developed, "improved" force fields based on ALL 71 and EAS do now give correct predictions for **12**,[32] we have already expressed our reservations concerning this procedure. Application of the EFF-EHMO method to **12**, using the original EFFs, correctly predicts the BCB form to be more stable (Table I), and thus circumvents the need for reparametrization.

In several more recent studies on nonaromatic hydrocarbons, the EFF-EHMO method has also been found to reverse EFF predictions and to select the correct conformational ground states. For present purposes, it will suffice to summarize the role of the EFF-EHMO method in these studies; detailed reports will appear shortly. Extensive EFF calculations on 1,1,2,2-tetracyclohexylethane (**13**)[33] and *meso*-1,2-di-*tert*-butyl-1,2-bis(1-cyclohexenyl)ethane (**14**)[34] revealed several minima in each case. The X-ray structures of **13**[33] and **14**[34] were determined, and in each case the conformation was found not to correspond to the calculated EFF ground state, but rather to a higher energy EFF minimum. In contrast, EFF-EHMO calculations gave the correct ground-state conformation for both **13**[33] and **14**. In another study,[35] it was shown that EFF-EHMO calculated A-ring conformations in a series of steroids are consistent with experimental findings, whereas those from EFF calculations are not.

Our studies of aliphatic compounds have also led to the detection of another feature of the hybrid method. For corresponding conformations calculated by different force fields, EFF-EHMO calculations tend to favor the structure with longer C-C single bonds. This result is not surprising, since EH geometry optimization of ethane produces a C-C bond length of 1.92 Å.[5a] Thus far, this feature has not been very influential in determinations of relative conformer energies, since most conformers have roughly the same bond lengths. However, it could become significant for highly strained structures.

Other Applications

Although our primary interest in the EFF-EHMO method is in relation to relative conformer energies, we have, in a preliminary way, tested the applicability of the method to some other types of problems. In the original EHT study,[5a] the tendency of EHT to overestimate steric effects was considered to result in incorrect relative energies for some constitutional isomers. For example, isopentane was predicted to be less stable than *n*-pentane.[5a] Since the EFF-EHMO method treats steric

Table III. Heats of Formation and Strain Energies Calculated by EFF-EHMO[a]

compd	ΔH_f ALL 71	ΔH_f EAS	ΔH_f exptl[b]	strain energy ALL 71	strain energy EAS	strain energy exptl[c]
n-butane (**9**)	−29.52	−31.15	−30.60	0.84	−0.79	−0.24
methylcyclohexane (**10**)	−36.40	−38.43	−36.98	1.46	−0.57	0.88
trans-decalin	−43.21	−47.22	−43.52	2.15	−1.86	1.84
cis-decalin	−43.01	−47.46	−40.43	2.35	−2.10	5.03
adamantane	−40.69	−49.34	−30.65	−1.27	−9.92	8.77
cyclodecane (**12**)	−39.44	−38.89	−36.29	11.86	12.41	15.01
norbornane	−22.21	−18.73	−12.42	7.76	11.24	17.55
cubane	40.40	61.81	148.70	57.68	79.09	165.98
dodecahedrane	−37.60	−40.39		5.60	2.81	

[a] Values are in kcal/mol. [b] From the values listed in ref 29. [c] Calculated from the appropriate ΔH_f and the strain-free group increments of Schleyer (ref 29).

effects very differently from EHT (see above), we examined several simple systems of constitutional isomers. The results (Table II) clearly demonstrate that the performance of the hybrid method is no better than that of EHT in this respect. In all three cases, the conformer energies are incorrectly ordered. We are therefore forced to conclude that the EFF-EHMO method is no more reliable than EHT in determining relative energies of constitutional isomers. It seems likely that this is the result of an intrinsic flaw in EHT, rather than of an overestimation (or underestimation) of steric effects.

The data at hand allow for a simple calculation of the heat of formation and strain energy of any compound, using the appropriate homodesmotic reaction[36] and the heats of formation of several simple molecules. For example, for methylcyclohexane (**10**), EFF-EHMO energies are used to calculate the ΔH for the reaction in eq 1. Given this quantity and the heats of formation for ethane, propane, and isobutane, the ΔH_f for **10** can be easily obtained,[37,38] and thence a strain energy can be calculated using standard, strain-free group increments.[29,39]

$$\underset{\mathbf{10}}{(CH_2)_5CHCH_3} + 6CH_3CH_3 \rightarrow 5CH_3CH_2CH_3 + (CH_3)_3CH \quad (1)$$

Table III summarizes the ΔH_f and strain energy calculations performed on a small but representative sampling of molecules. For the relatively unstrained molecules **9–11**, the EFF-EHMO method yields a fairly accurate prediction of ΔH_f. This result is not unexpected, since it had previously been shown that EH bond energies are roughly additive.[5a] In the same study it had been concluded[5a] that EHT fails to predict strain energies in cyclic compounds. Our results (Table III) show that, given adequate geometries, EHT does produce appreciable strain energies, although the magnitudes are consistently underestimated. Despite this tendency, the almost complete absence of strain predicted for dodecahedrane (Table III) is of some interest. EFF calculations of the strain energy of this molecule are strongly force field dependent, with reported values of 43 and 88 kcal/mol for the EAS and ALL 71 EFFs, respectively.[29] The EFF-EHMO results favor the EAS estimate, as do recent experimental findings.[40]

Conclusion

It is now well established that the EFF method can be of considerable value in the conformational analysis of large molecules, despite its lack of a firm theoretical foundation. The relative stabilities of conformers as calculated by this method are generally reliable, as long as the energy differences are sizable. When this is not the case, the EFF-EHMO method provides an additional guide to the selection of the most stable conformer. Although, as is true of any empirical method, EFF-EHMO results must be interpreted with some caution, we believe that the findings of the present study demonstrate the usefulness of this novel hybrid approach.

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(6) Recent work[7] has shown that the sum of the one-electron energies, the energetic quantity produced by EHT, can be empirically related to the total energy of a molecule by a multiplicative factor of $^3/_2$. This result suggests that relative energies obtained by the EFF-EHMO method should be multiplied by $^3/_2$. However, we have refrained from applying this correction, since such energy values are of qualitative significance only.

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(19) The results in Figure 1 were obtained as follows. The ring dihedral angles (ϕ) were fixed at preset values which enforced the presence of an S_4 axis; this was achieved by assigning a torsional function of the form $E = 10000(\phi - \phi_0)^2$ (E in kcal/mol, ϕ in radians, for a definition of ϕ, cf. ref 15). All other geometric parameters were relaxed by use of the previously described[8] EFF. The energies of the structures thus obtained were computed by the EH method.

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(24) In our earlier study[22] we were primarily concerned with the central bond length of **8**, and in this respect the EFF prediction is in excellent agreement with experiment (calcd[22] 1.595 Å; found[23] 1.606 Å).

(25) See ref 22 for a definition of ϕ_r and ϕ_c.

(26) To demonstrate that a significant energy barrier separates **8a** and **8c**, the values of ϕ_r and ϕ_c for each form were transformed in a direction toward the corresponding values for the other minimum. Upon relaxation, these two new structures returned to the minima from which they were derived. This procedure did modify the structure of **8** slightly from that reported in ref 22.

(27) We have noticed this phenomenon in other cases. For example, an extensive search[28] of the hyperspace of gauche **5** has uncovered seven gauche minima, four more than previously[20b] reported. (However, all new gauche minima were more than 5 kcal/mol higher in energy than the anti ground state.)

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(38) The following EFF-EHMO energies (eV) are required for homodesmotic reactions using the ALL 71 (or EAS) EFF; ethane, −248.1214 (−248.0490); propane, −353.9602 (−353.8723); isobutane, −459.7384 (−459.6363); neopentane, −565.4519 (−565.3359).

(39) Alternatively, the strain energy of a molecule may be considered to equal $-\Delta H$ for the appropriate homodesmotic reaction. This approach leads to essentially the same results using the EFF-EHMO method, except that the strain energies are generally several kilocalories per mole smaller.

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Excited-State Spectroscopy of Hexacyanocobaltate(III)

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Abstract: The hexacyanocobaltate(III) anion, dissolved in an EPA matrix at 94 K, gives rise to a well-structured transient spectrum in the 365-500-nm range. By means of a straightforward ligand field analysis the observed absorbance could be identified as the absorption spectrum of an excited $^3T_{1g}$ state of the complex. Transitions to several components of a triplet cluster, arising from a $(t_{2g})^4(e_g)^2$ configuration, were assigned. The interpretation is shown to be consistent with the luminescence properties of this species. The present data allow for a direct electronic characterization of a relaxed excited state. The relevance of our results to the photochemistry of trivalent cobaltum compounds is discussed.

Introduction

The absorption spectrum of an excited state offers an unusual, but quite instructive, view of the energy level pattern of a given molecule. A number of other excited states, that are otherwise inaccessible from the ground state (due to selection rules, for instance), may now become observable. In some cases, the excited state relaxes into a metastable species, characterized by a novel geometrical structure. Obviously, the excited-state spectrum constitutes one of the major keys in elucidating this structure; moreover, it can be expected to contribute significantly to the understanding of the photophysics and the photochemistry of the molecule under consideration.

In transition-metal chemistry, only a very limited number of transient spectra have been observed;[2] so far, especially Cr(III) complexes have been studied.[3-6] Indeed, it has been found that these d^3 systems can be further excited from their lowest excited doublet states. As these doublet states belong essentially to the same $t_{2g}{}^3$ electronic configuration as the quartet ground state, one does not anticipate a large change in geometry. The spectral assignments are still controversial.

Virtually no data are available at present for the important class of d^6 complexes (Co(III), Rh(III), Ru(II), Fe(II)), except for a report on $[Ru(bpy)_3]^{2+}$, where a triplet charge transfer state is supposed to give rise to a triplet-triplet absorption peak,[7] and for a preliminary communication by Adamson and co-workers[8] on $Rh(NH_3)_5Cl^{2+}$.

In this note, we present the excited state absorption spectrum of hexacyanocobaltate(III), measured at low temperature in a glass matrix. We suggest a straightforward identification of the observed bands in the framework of a ligand field model.

Experimental Section

A 3×10^{-2} M solution of $[(C_4H_9)_4N]_3Co(CN)_6$ in EPA was prepared in the dark and pipetted into a quartz 1 × 1 × 4 cm spectrophotometer cell. The cell was suspended in an all-quartz Dewar, equipped with three sets of flat windows. The sample was cooled by means of a stream of cold nitrogen gas.

The excitation system consisted of a 2000 JK Lasers Ltd. Q switched ruby laser with frequency doubler. The system has an output at 347 nm of 270 mJ in 30 ns. The beam cross section is 4 × 8 mm.

A 250-W stabilized xenon arc was used as the source of the detection light. It was passed through the sample at an angle of 90° with respect to the direction of excitation. The cross section of the detection beam was limited so as to probe only the volume contained in the first 1 mm irradiated by the exciting light. Since the laser light was appreciably absorbed by the sample, this volume contained the largest concentration of excited species.

Absorbance changes were detected through a Jobin Yvon HD 20 monochromator by means of a 1P28A photomultiplier and a type 476 Tektronix oscilloscope.

The present data were recorded at a temperature of 94 K. Ab-

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