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Ab initio calculations on the *o*-benzyne–Ar and *o*-benzyne–CO complexes

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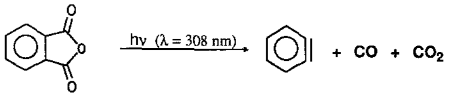
Summary. Van der Waals complexes of *o*-benzyne with carbon monoxide and with argon have been studied *ab initio*. In both cases "sandwich" structures were found to be more stable than planar structures. From the order of stability of the planar structures it was concluded that the classical description of the distorted triple bond in *o*-benzyne is not fully valid, and it is believed that one must also consider the biradical character of the triple bond in *o*-benzyne.

Key words: Ab initio – vdW complexes – Benzyne

I Introduction

The remarkable development of organic chemistry for years has been facilitated by the skillful exploitation of numerous empirical rules which were obtained by generalizations derived from a vast amount of experimental data. Sometimes, however, failure of these rules has proved to be more exciting than their successes. Specifically, a strictly linear arrangement of CC triple bonds and of cumulated double bonds is well established. About 30 years ago an unusual molecule, *o*-benzyne, was prepared at low temperature in an inert matrix which violated the rule of linearity of a system containing a CC triple bond [1].

Recently several quantum chemical studies have dealt with *o*-benzyne and related systems [2–5] and proved very useful in the interpretation of the high-resolution, single-site IR spectrum of *o*-benzyne and of its isotopomers [2] as well as the electronic absorption spectrum of *o*-benzyne [5]. *o*-Benzyne was formed by the classical photochemical decomposition of phthalic anhydride (reaction 1) in an inert matrix at 4 or 10 K.



(1)

Dedicated to Prof. Dr. Werner Kutzelnigg on the occasion of his 60th birthday

The photochemical decomposition of phthalic anhydride located in an argon cavity presumably leads to a substantial increase of the van der Waals' (vdW) volume and results in serious overcrowding. Since the compressibility of the surroundings is negligible, high static pressure is created in the cavity. This congestion can be relaxed by a slight warming of the matrix and is accompanied by dramatic changes in the complicated line-shape of each infrared absorption of *o*-benzyne, CO and CO_2 [2]. While trying to understand these spectra, it occurred to us that vdW complexes (in particular the one of *o*-benzyne and CO) might be involved and might play a role in the photoinduced carbonylation of *o*-benzyne. While exact simulations of spectra in the condensed phase are at present obviously out of the question, we considered it expedient to calculate interaction energies of the formation of vdW complexes between *o*-benzyne and an argon atom and a CO molecule.

Additional motivation for this study came from a recent, extensive investigation of benzene complexes [6–9]. We hoped that comparison of these two related systems might help us to understand better the unique features of the electronic structure of *o*-benzyne introduced by an additional bond. Dispersion energy, i.e., correlation energy, accounts for all the stabilization of the *o*-benzyne–Ar and almost all the stabilization of *o*-benzyne–Co van der Waals' molecules. The induction energy (included in the SCF interaction energy) due to the polarization of Ar or CO by the benzyne dipole is extremely small. Both complexes must therefore be studied theoretically by means in which correlation is taken into account. The size of these complexes prevents the use of the most sophisticated methods (e.g. coupled cluster or complete active space) which would include a larger portion of the correlation energy. However, Moller–Plesset (MP) theory [10] performed through the second-order (MP2) accounts for a reasonable portion of the correlation energy, and most importantly it is practical for the large complexes under study here. Moreover, recently we have investigated at the same level the structurally related benzene–X (X = benzene [6]; Ar [7]; He, Ne, Ar, Kr, Xe [8]; N_2 [9]) van der Waals molecules. This gives us a unique chance to compare the benzene–X complexes with their *o*-benzyne analogous. Theoretical characteristics of the benzene–X complexes agree fairly well with available experimental values [6–9]. This validates the choice of the theoretical procedure, and the results obtained for the present complexes, for which experimental results are not available, might be considered as reliable.

II Calculations

The interaction energy (ΔE) of complexes, determined at the MP2 level, consists of SCF and correlation (COR) contributions,

$$\Delta E = \Delta E^{\mathrm{SCF}} + \Delta E^{\mathrm{COR}} \tag{1}$$

Both terms were corrected for the basis set superposition error using the function-counterpoise method of Boys and Bernardi [11]. All of the occupied and virtual orbitals of the "ghost" system were used. A detailed discussion of this procedure is given in Ref. [12]. We would like to mention here that recent studies [13–15] give convincing evidence that there is not any overcorrection in the original function counterpoise procedure; this conclusion was based on formal as well numerical results.

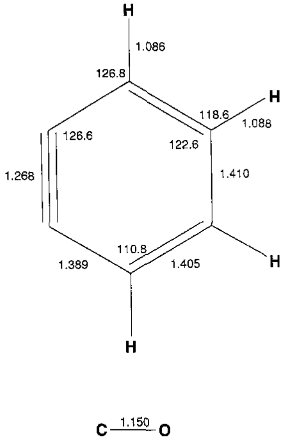


Fig. 1. MP2/6–31 G* optimized geometries of *o*-benzyne and CO molecules; bond lengths in Å, angles in degrees

In our previous papers [6–9] the experimental subsystem geometry was used. Since the experimental geometry of *o*-benzyne is not available, the theoretical geometries for both *o*-benzyne and CO were used. The geometries were obtained in both cases by means of gradient optimization at the MP2/6–31 G* level (see Fig. 1).

The subsystem geometries were kept rigid during optimization and only the position of Ar or CO were varied. This means the internal relaxation of the *o*-benzyne is neglected. Such an approach is used routinely in case of neutral molecular complexes, and even in the case of H-bonded complexes it provides correct values of interaction energy. We have estimated [16] the effect of internal relaxation in case of the T-shaped benzene dimer. Using gradient optimization we have shown that subsystem relaxation increased the stabilization energy of the dimer only marginaly, by less than 0.01 kcal/mol. Because the present complexes are weaker than the benzene dimer, we can safely expect that the internal relaxation will be negligible for the present complexes. Furthermore the complete gradient optimization at the theoretical level used is hardly feasible. Moreover due to problems with the superposition error, it does not provide correct characteristics of the complexes under study. Altogether six initial structures of the *o*-benzyne–Ar complex and six structures of the *o*-benzyne–CO complex were studied. They all are shown in Figs. 2 and 3.

Two different basis sets were used for the subsystem geometry optimizations and for the evaluation of the interaction energies. Standard basis sets are adequate for the former, while the latter requires addition of diffuse functions. For the *o*-benzyne and CO geometry optimization, the standard 6–31 G* basis set was used. For the evaluation of the interaction energy these basis sets were modified. The reason for the modification is that it is known the standard 6–31 G* basis set underestimates interaction energies [17]. Two modifications were made:

(i) the diffuse *sp*-shell was added for the carbon and oxygen atoms with exponents 0.056 and 0.09, respectively. This represents 1/3 of the exponent value for the outermost sp shell for these atoms;

(ii) the standard *d*-functions on C and O atoms ($\alpha = 0.8$) were replaced by a more diffuse function with an exponent equal to 0.25.

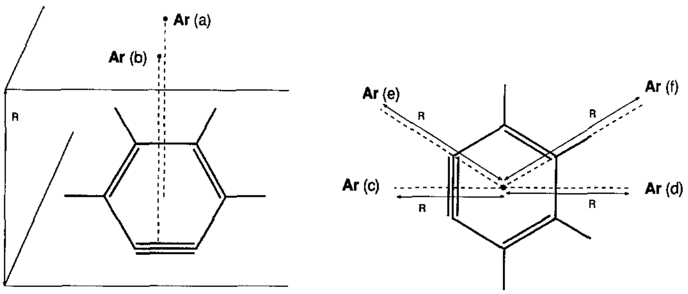


Fig. 2. Assumed structures for *o*-benzyne–Ar. In the sandwich structures (a) and (b), the intermolecular distance *R* is taken as the distance between parallel molecular planes. Intermolecular separation in the planar structures (c) and (d) is given by the distance of between centers of mass and, finally, intermolecular separation in the planar structures (e) and (f) corresponds to the distance between argon and adjacent carbon atoms

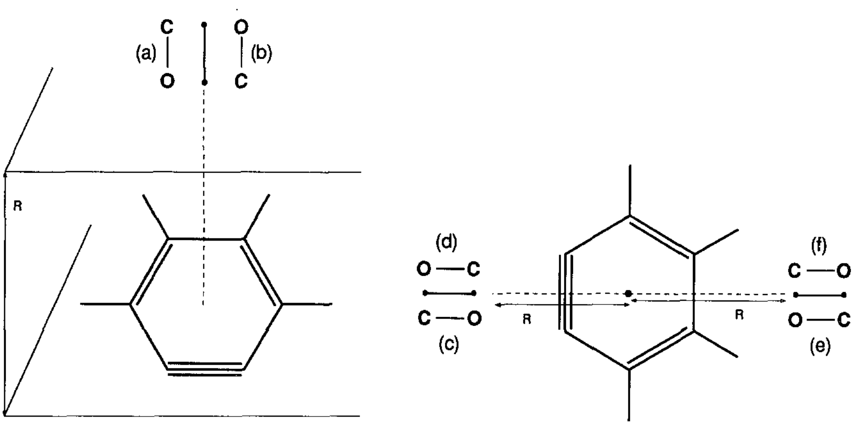


Fig. 3. Assumed structures for *o*-benzyne–CO. In the sandwich structures (a) and (b) the CO molecule lies on the axis which is perpendicular to the *o*-benzyne plane with either O and C atoms closer to the *o*-benzyne ring; the intermolecular separation *R* is taken as the distance between the O and C atoms and the center of mass of *o*-benzyne. Intermolecular separation in the planar structures (c), (d), (e) and (f) is taken as the distance between C, O, and O, atoms with the center of *o*-benzyne

The use of the diffuse *sp*-shells and *d*-functions has been recommended in Refs. 12 and 13. The resulting 6–31 + G* (0.25) basis set gives fairly good values of the polarizability and quadrupole moment of benzene. For the argon atom the [7*s*4*p*2*d*1*f*] basis set [20] was used; the exponents of *d* functions (0.84 and 0.174) and of *f* functions (0.23) had been optimized [20] with respect to dispersion energy.

III Results and discussion

A Isolated subsystems

The MP2/6–31 G* optimized geometries of the subsystem of *o*-benzyne and CO are summarized in Fig. 1. The MP2/6–31 G* and MP2/6–31 + G* (0.25) dipole

Table 1. Interaction energies (in kcal/mol) for various structures of the *o*-benzyne–Ar complex.

R(Å)	Structure[a]					
	a	b	c	d	e	f
2.5						
3.0	0.407	0.323				
3.1	− 0.331					
3.2	− 0.790					
3.3	− 1.054					
3.4	− 1.184	0.808				
3.5	− 1.224	− 0.907	27.032		− 0.518	
3.6	− 1.206	− 0.939				0.670
3.7		− 0.927			− 0.527	
3.8	− 1.079	− 0.887	9.733			
4.0	− 0.907				− 0.440	
4.1			2.923			− 0.289
4.4			0.469			
4.5	− 0.529	− 0.446				
4.6			− 0.136	0.279		− 0.260
4.7			− 0.285			
4.8			− 0.372	− 0.281		
4.9			− 0.415			
5.0			− 0.431	− 0.467		
5.1			− 0.426	− 0.490		− 0.160
5.2			− 0.410	− 0.487		
5.5	− 0.170		− 0.332	− 0.406		
6.0			− 0.206	− 0.247		
7.0			− 0.074			

[a] See Fig. 1; distance R refers to the distance between two parallel planes (structures a, b), or to the distance between Ar and the center of mass of *o*-benzyne (structures c, d) or to the distance between argon and the adjacent carbon atom (structures c, f).

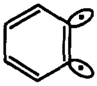
moments of CO are − 0.453 and − 0.550 D, respectively (carbon atom bears a negative charge). The orientation of the dipole is reversed when passing from SCF to MP2. The MP2/6–31 G* and MP2/6–31 + G* (0.25) dipole moments of *o*-benzyne amount to 1.707 and 1.916 D, respectively (with negative charge on carbon atoms in the triple bond). Contrary to the previous case, the orientation of the *o*-benzyne dipole is not changed when passing from SCF to MP2 level.

The polarizability of *o*-benzyne evaluated at the HF/6–31 + G* (0.25) level is equal to 65.8 a.u.^{3}; this value is slightly smaller than that of benzene evaluated at the same level (66.5 a.u.^{3}, Ref. 2). The lower polarizability of *o*-benzyne is not surprising. Additive summation of bond polarizabilities gives a lower total polarizability for *o*-benzyne (by about 1.5% in comparison with the total polarizability of benzene). Investigating the in-plane components of *o*-benzyne polarizability we found, in agreement with expectation, a larger value for the y-component than for the x one (85.4 a.u.^{3} and 71.2 a.u.^{3}, respectively). The x axis coincides with the C_{2v} axis (cf. Fig. 1). The perpendicular z-component is smaller (41 a.u.^{3}) than the in-plane components. The corresponding values found for benzene are 78.2, 78.2 and 43.8 a.u.^{3}, respectively. The fact that the y-component of polarizability is larger than the x one indicates that the approach of the second subsystem along the x axis may be energetically less favourable than that along the y axis. This is valid providing the dispersion contribution represents the dominant attractive term.

B Complexes

o-benzyne–Ar. The total stabilization energies ΔE, defined by Eq. 1, are presented in Table 1. For all the structures (supersystems) studied the stabilization comes exclusively from correlation effects since the SCF interaction energy is repulsive. Only at large distances (5.5–7 Å) was a very small SCF stabilization (0.001–0.002 kcal/mol) found. The correlation interaction energy results mainly from the classical London dispersion energy which is proportional to the sixth power of the reciprocal distance between the subsystems and to the polarizabilities of both subsystems. For the forthcoming discussion, we will mention that polarizability of *o*-benzyne is not isotropic and regions with higher electron density possess higher local polarizability.

Of the six *o*-benzyne–Ar structures investigated, the sandwich structure a is the most stable and is followed by another sandwich structure b. Sandwich structure refers to a structure where *o*-benzyne and Ar are located in parallel planes. Structure e in Fig. 2 (– 0.527 kcal/mol) is the most stable among the planar structures studied, and is followed by structure d (– 0.490 kcal/mol) and c (– 0.431 kcal/mol). All these interaction energies represent typical van der Waals values, and it is seen that the differences among them are not very large. However, we have to admit that our original expectation, based on experience, was somewhat different. "Clouds" of π-electrons above and below the ring plane in *o*-benzyne are responsible for significant stabilization of sandwich-type complexes; this is in agreement with calculations for benzene as well as *o*-benzyne. For the same reason we expected, within the framework of planar approaches, the largest stabilization for structure c, which is not the case according to our calculations. Energetically the most favoured approach is that one labeled e, which supports the biradical nature of *o*-benzyne. The formal representation in formula 1 is very probably not exactly correct because no electron spin resonance signal, characteristic of the localized triplet, was detected in our samples. Although even this formula is not strictly speaking acceptable, the preference of structure e over c suggests its "partial" validity. To prove this conclusion we have performed CASSCF calculations for six electrons and six active orbitals (6–31 G* basis; MP2/6–31 G* geometry). The single determinant Hartree–Fock description was really found to be rather poor. The large expansion coefficient (0.2660) of the doubly-excited configuration supports a partial biradical character of *o*-benzyne. This conclusion fully agrees with results of CASSCF calculations in Ref. 5. Again, in contrast to our expectation, structure d is slightly preferred over c. What is remarkable to us is the absence of exchange repulsion due to the two hydrogen atoms which are known to act merely as repulsion centers.



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In order to shed more light on this problem we have calculated also the acetylene–Ar "sandwich" (C_{2v}) complex at the same theoretical level and with the

Table 2. Interaction energies (in kcal/mol) for various structures of the *o*-benzyne–CO complex.

R(Å)	Structure[a]					
	a	b	c	d	e	f
2.9		0.347	90.124			
3.0	– 0.869					
3.1						
3.2	– 1.037	– 0.566	35.694			
3.3	– 1.027	– 0.649				
3.4	– 0.984	– 0.675				
3.5		– 0.662	13.163	27.901		
3.6		– 0.626				
3.8	– 0.706	– 0.518	4.351			
4.1		– 0.344		4.710		
4.3	– 0.407					1.866
4.4		– 0.206	0.0	1.825	– 0.014	
4.7		– 0.112		0.671		– 0.352
4.8	– 0.233		– 0.322		– 0.488	
4.9					– 0.488	
5.0		– 0.052	– 0.322	0.244	– 0.471	– 0.695
5.15						– 0.712
5.2					– 0.409	
5.3	– 0.138	– 0.016		0.104		– 0.684
5.6			– 0.218	0.065	– 0.282	
5.8				0.060		
6.0					– 0.184	
6.2				0.062		
7.0			– 0.068		– 0.063	
8.0				0.053		

[a] See Fig. 2; distance R refers to the distance between O or C aroms and the *o*-benzyne plane (structures a, b), or to the distance between O, C and O atoms and the center of *o*-benzyne molecule (structures c, d, e, f).

same basis sets. For the optimal distances found for structure b, i.e. 3.6 Å, we obtained a much smaller MP2 interaction energy (– 0.146 kcal/mol). Comparing SCF and correlation interaction energies for the acetylene–Ar and *o*-benzyne–Ar complexes we found that the former contributions are almost identical (0.869 and 0.805 kcal/mol), while the latter ones differ significantly (– 1.015 and – 1.744 kcal/mol). This means that the polarizability (and also electron density) in the C ≡ C region of *o*-benzyne is larger than that in acetylene.

Comparing the *o*-benzyne–Ar and benzene–Ar complexes we find sandwich structures a to be the most stable in both cases; stabilization energies and intermolecular distances are almost identical (ΔE – 1.226 kcal/mol, R = 3.526 Å for benzene–Ar, Ref. [3]). This is not surprising in light of the similar polarizabilities of *o*-benzyne and benzene (see above).

o-benzyne–CO. Stabilization energies obtained for various structures (cf. Fig. 3) of the complex are given in Table 2. The sandwich structure a is the most stable, the other sandwich structure b is less stable. Clearly, the interaction between the π-electrons of *o*-benzyne and a positively charged oxygen atom is responsible for the larger stabilization in the case of a. On the other hand the fact that a rather large stabilization energy was found for the structure b gives evidence about the important role of the correlation interaction energy and less important role of dipole–dipole electrostatic term which is included in the SCF interaction energy. The stabilization energy found for structure a is still slightly lower than that found for the most stable structure of *o*-benzyne–Ar. Of the four planar *o*-benzyne–CO structures, structure f is the most stable, and structure c is the least stable. Similarly as with the sandwich structures a and b, it is seemingly the electrostatic contribution which favors structure f. In accord with previous results for *o*-benzyne–Ar, the planar structures c and d are less stable than structures e and f; for the structure d even no minimum was found.

Conclusions

We have investigated theoretically complexes of *o*-benzyne with Ar and CO. In both cases we find that sandwich structures are the most stable. The former complex is more stable than the latter one despite the attractive electrostatic contribution present in the latter complex only. From the order of stability of the planar structures of *o*-benzyne–Ar and CO we find it apparent that the classical description of the distorted triple bond in *o*-benzyne is not fully valid, and its partial biradical character has to be considered. The partial biradical character of *o*-benzyne was supported by the CASSCF calculations. For both complexes the preferred planar structures do not correspond to the expected ones, i.e., those were Ar and CO are approaching the $C \equiv C$ region of *o*-benzyne. In fact both subsystems prefer to approach from the opposite side of *o*-benzyne. From the investigated structures of *o*-benzyne–CO complex we conclude that the electrostatic contribution is rather important.

We hope that these results will stimulate further experimental effort aimed both at a better understanding of the electronic structure of this intriguing molecule and its vdW complexes.

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