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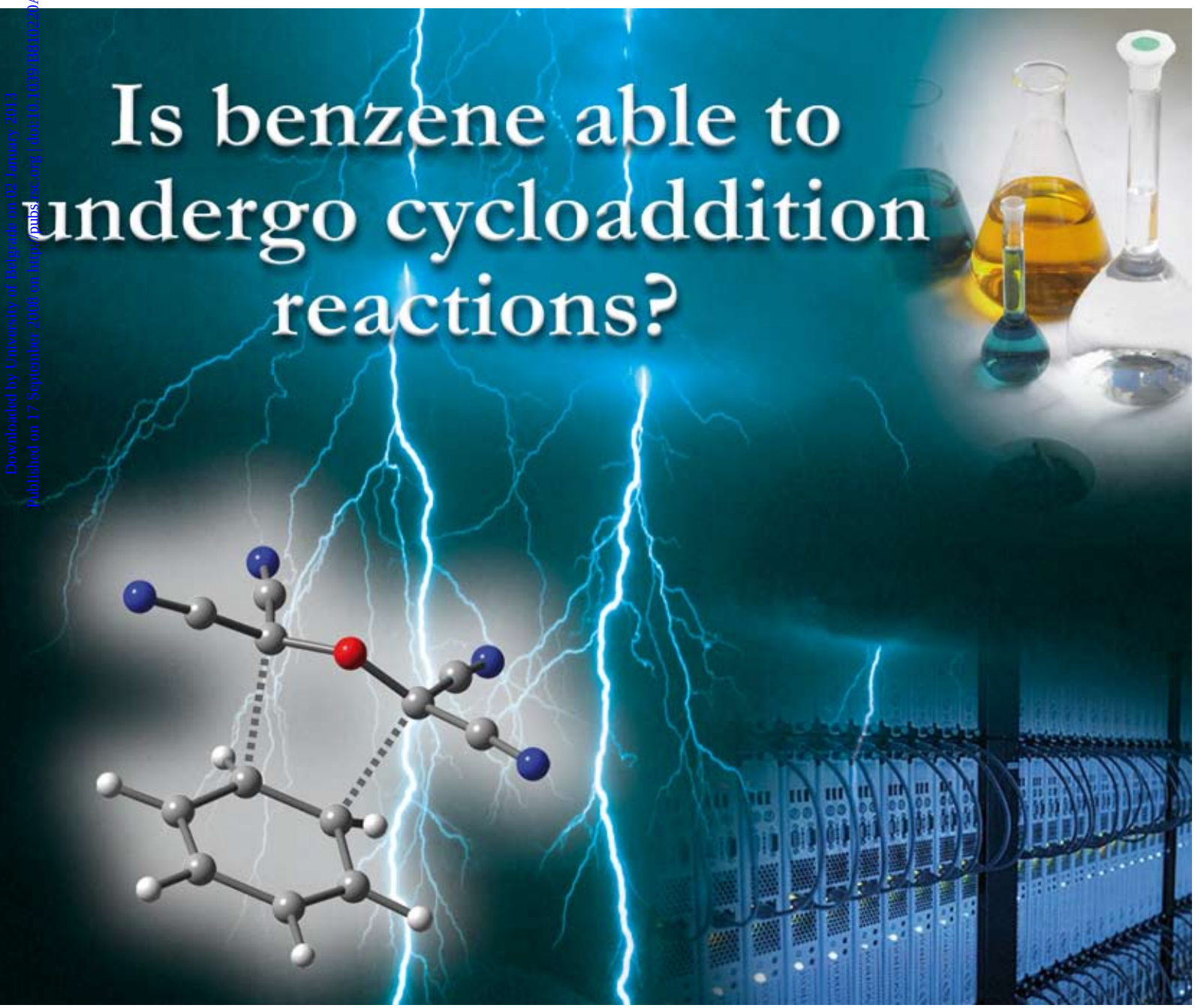

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PAPER

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The unusual reactivity of benzene and monosubstituted benzenes towards tetracyanoethylene oxide: a theoretical study

The unusual reactivity of benzene and monosubstituted benzenes towards tetracyanoethylene oxide: a theoretical study†

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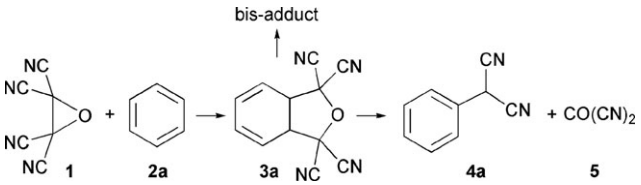
The cycloaddition of tetracyanoethylene oxide (TCNEO) with benzene and benzene derivatives, and the subsequent evolution of the corresponding cycloadducts is theoretically investigated using DFT and highly correlated *ab initio* calculations. Both the relative reactivity of the different aromatic compounds, as well as the regioselectivity of the cycloaddition is explained in light of the theoretical study. Insights in the formation of arylmalononitriles, which gives potential synthetic applications to this process, are also offered.

Introduction

As the prototypical aromatic compound,[1,2] benzene is not expected (in the ground-state) to behave like an olefin towards dienes or 1,3-dipoles, neither like a diene towards olefins. This is the reason why benzene and toluene are often used as solvents in cycloaddition reactions. Some exceptions of Diels–Alder reactions involving benzene are known.[3–5] Apart from [4 + 2] cycloadditions, only ozone[6] and tetracyanoethylene oxide (TCNEO, **1**)[7–9] have been reported to react with benzene derivatives to give dihydrobenzotrioxoles and tetrahydroisobenzofurans, respectively. Although the cycloaddition of ozone to benzene derivatives has been studied on both experimental[6] and theoretical[10] basis due to its importance in atmospheric chemistry, the reaction with TCNEO has not received the same level of attention despite its mechanistically challenging nature and synthetic relevance. In this sense, although the reaction was discovered in the 1960s,[7,8] it remained relatively unexplored until 1992, when a more detailed experimental study was carried out employing a broader range of substituted benzenes.[9] We will now summarize some of the recent experimental results obtained with benzene **2a**[7] (Scheme 1) and those we have obtained with toluene **2b**, fluorobenzene **2c**, chlorobenzene **2d**, anisole **2e** and nitrobenzene **2f** (Scheme 2),[9] leaving aside the formation of bis-adducts.[7–9] It should be noted that after the cycloaddition, the corresponding monoadducts (generally labeled as **3**) can open in two ways, namely a and b depending on the relative positions of the fragmented $CO(CN)_2$ unit and the benzene substituent, as displayed in Scheme 3.

According to the observed distribution of regioisomers,[9] it seems that in all cases the C–C bond proximal to the R group



Scheme 1 The whole process in the case of benzene as dipolarophile.

is preferentially broken. This means that the *ortho* monoadduct (**3o**) opens into the *meta* arylmalononitrile (**4m**) while the *meta* (**3m**) opens into the *para* (**4p**). For instance, in the case of the methoxy-substituted species, **4em** and **4ep** should derive from **3eo** and **3em**, respectively, although any of these monoadducts could be isolated.[9] Since no **4em** is observed, probably there is no **3eo** formed in the first step and the reaction of TCNEO with anisole is, therefore, highly or totally regioselective.

With all these experimental results in mind, we have undertaken a systematic computational mechanistic study through *ab initio* and DFT calculations in order to get more mechanistic insights on this rather unusual reaction schemes and to better understand the origin of the observed selectivities.

Results and discussion

The activation of TCNEO (1)

The first stage of the computational study deals with the formation of the active form of **1** which, as suggested in very early works,[11] is the tetracyanocarbonyl ylide open form **1′** (Scheme 4(a)). The electronic nature of this substrate has traditionally been a subject of speculation and **1′** cannot be considered a prototypical 1,3-dipole due to its C_{2v} symmetric character and the high delocalization of its charge by the four nitrile groups. As a consequence, a high number of resonance structures can be written as depicted in Scheme 4(b). Evidences arising from experimental studies of the addition of **1** to olefins indicate that **1′** has very little ionic character at all, because solvent and substituent effects on the reacting olefins would be much more pronounced if ions were involved.[11] Therefore, it

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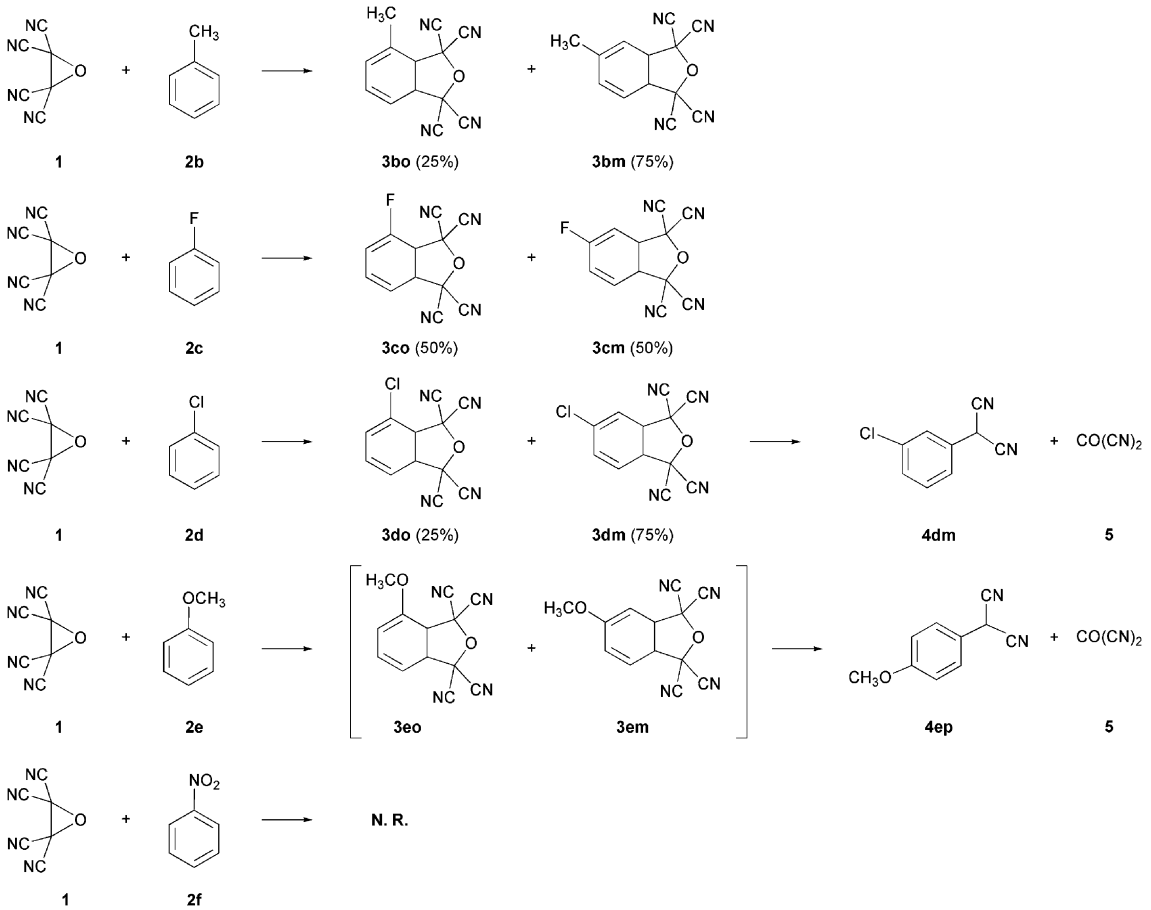
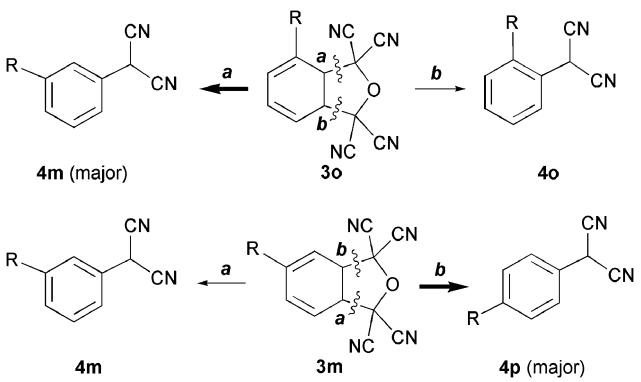
† Electronic supplementary information (ESI) available: Tables of electronic energies, as well as enthalpies, entropies, Gibbs free energies (the last three data series at 25 °C) and lowest frequencies for the different conformations of the structures considered in this work. Cartesian coordinates of the structures discussed in the paper. See DOI: 10.1039/b810220a



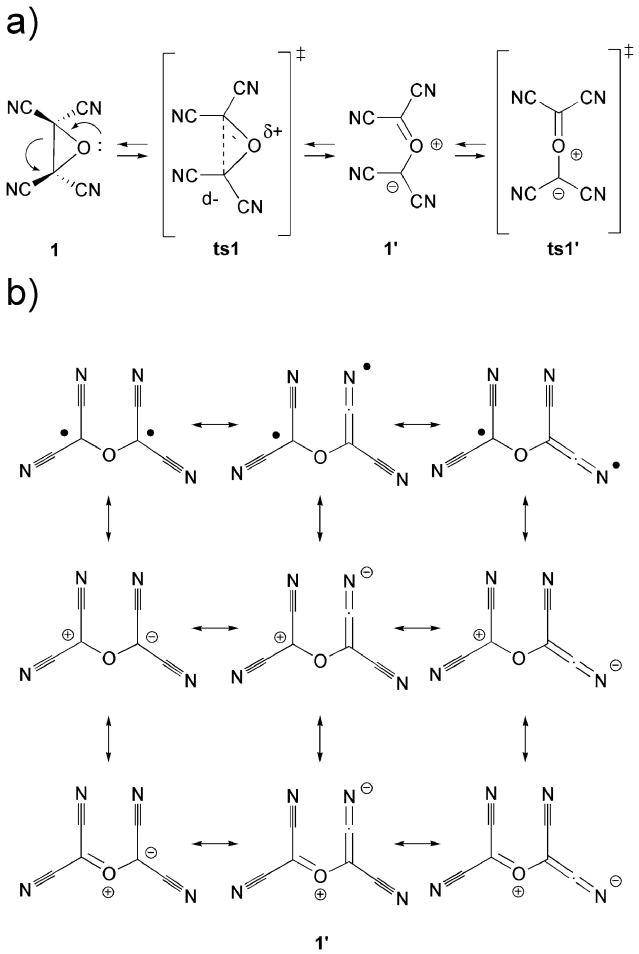
Scheme 2 The reaction in the case of monosubstituted benzenes.



Scheme 3 The ring opening (fragmentation) of the monoadducts into arylmalononitrile.

was proposed that tetracyanocarbonyl ylide **1′** should be qualitatively best described as a hybrid of zwitterionic and singlet biradical species (Scheme 4). In this sense, we first evaluated the structural and electronic properties of the open form of **1**. The relative energies of all the calculated structures are summarized in Table 1.

It was found that, in accord with previous results[12,13] this active species is formed in the ground state through a concerted, conrotatory ring opening of **1**, whose transition state (TS) **ts1** is 21.6 (UB3LYP) or 34.2 [CCSD(T)] kcal mol^{-1} above the cyclic form, indicating a relatively easy process. The corresponding open form **1′** is 8.7 (UB3LYP) or 21.8 [CCSD(T)] kcal mol^{-1} above the cyclic form, so its proportion in the reaction mixture must be very low. From a geometric point of view, **1′** has a C_{2v} symmetric planar structure as calculated with both restricted and unrestricted B3LYP, with O–C bonds being *ca.* 0.1 Å shorter with respect to those present in the closed form **1** and a wide open C–O–C bond angle of 133°. Natural population analysis of the charge distribution performed at the UB3LYP/6-31G(d) level reveals that the oxygen atom of **1′** carries a negative charge of −0.34 electrons and the adjacent carbons each a positive charge of +0.18. The nitrile groups distribute their charge equally between the C (*ca.* +0.2) and N atoms (*ca.* −0.2). This distribution is different to that shown by the parent carbonyl ylide at the same level of theory, in which the oxygen atom is also negatively charged (−0.40 electrons), but the methylene carbons each bear a negative charge of −0.16 and all the positive charge is distributed among the four hydrogens (*ca.* +0.2). These results point to an electronically different and highly delocalized average structure for **1′**, as further confirmed by its opposite (but also very low) calculated dipole moment of 0.70 D (0.61 D in carbonyl ylide). The transition structure corresponding to the linearization of the C–O–C bond was also located (**ts1′**) and it is 12.4 (UB3LYP) or 15.3 [CCSD(T)] kcal mol^{-1} above the bent form.



Scheme 4 (a) The conrotatory ring opening of **1** leading to the active planar form **1′** (only the heterolytic cleavage is shown) and (b) representative zwitterionic/singlet biradical resonance structures forms of **1′**.

On the other hand, CAS(6,6) single-point calculations showed 7% biradical character for cyclic **1**, 36% for **1′** (in accord with the 38% referred in the literature for unsubstituted carbonyl ylide[12,14]), 48% for **ts1** and 7% for **ts1′**. As in aforementioned previous studies,[13] the small level of biradical character in **1′** made the UB3LYP/6-31G(d) geometries and energies to be very similar to those calculated through the closed-shell variant. A good general agreement was obtained within the three theoretical methods, although the well-known tendency of DFT methods to overestimate the relative stability of partially biradical species (*i.e.* **ts1** and **1′**) with respect to correlated *ab initio* methods is revealed.

Cycloaddition of tetracyanocarbonyl ylide (1′) to benzene: mechanism

The calculated reaction mechanism has two key steps, responsible for the formation of the cycloadducts and their subsequent transformation into the corresponding arylmalononitriles through a formal cycloreversion. There are also two minor steps dealing with the aforementioned activation of **1** and the final protonation step, necessary to form the arylmalononitrile products. The global reaction pathway for benzene (**2a**) is shown in Scheme 5.

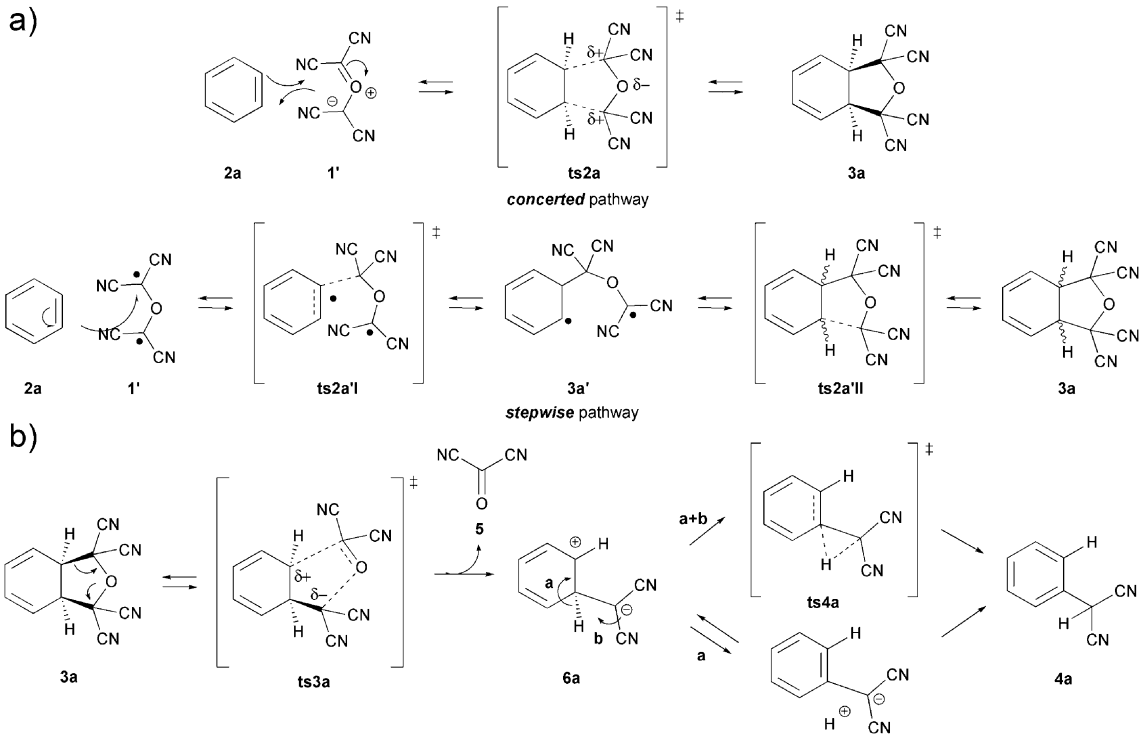
Concerning the first cycloaddition step, and given the moderate biradical character of **1′**, the possibility of two possible pathways, namely the concerted and stepwise ones, arise and should be considered. In this sense, experimental studies demonstrated that the reaction of **1′** towards olefins is very similar to the Diels–Alder and 1,3-dipolar cycloadditions, being thermal in nature and relatively insensitive to solvent effects and structural changes. The stereochemical studies showed that both new bonds are formed simultaneously or very nearly so. Another similarity with dipolar additions found was the faster reaction rate with the *trans* isomer of a *cis*/*trans* pair of olefins,[11] which has been traditionally postulated as a criterion of a multicentered process. All these findings are characteristic of cyclic reactions which are "concerted" or "nearly concerted".

When looking at previous theoretical studies on similar processes, it is found that, although the electronic structure and reactions of carbonyl ylides ("push–pull" stabilized or not) with olefins (mainly ethylene) has been calculated,[15–17] these studies were mostly carried out through semiempirical and low-level *ab initio*/DFT methods in a sense that comparison with experiments was not always possible. For example, MINDO/3 computations on the cycloaddition of carbonyl ylide to ethylene gave that the stepwise transition state is about 17 kcal mol^{-1} lower in energy than the other synchronous pathways found at the same level.[16] In contrast, other studies were performed directly under closed-shell conditions without considering the stepwise mechanism.[17] More sophisticated theoretical studies have been done to investigate the mechanism of the addition of thiocarbonyl ylides[13] to ethene and thiocarbonyl compounds. These studies found that, although biradical pathways are amenable, they require activation energies not competitive with the four-center pathways. However, the authors suggested that competition between the concerted and stepwise modes of cycloaddition might favor a biradical pathway if radical-stabilizing substituents were introduced in the reactants (which in turn is much more difficult to achieve when going from

Table 1 Calculated relative zero-point corrected energies (in kcal mol^{-1}) and percentage biradical character of various structures located in the tetracyanoethylene oxide–tetracyanocarbonyl ylide potential energy surface, according to different levels of *ab initio*/DFT calculations

Structure	B3LYP[a]	UB3LYP[a]	CAS(6,6)[a]	CCSD(T)[b]	% BRC
1	0.0	0.0	0.0	0.0	7
ts1	27.8	21.6	35.4	34.2	48
1′	9.8	8.7	23.9	21.8	36
ts1′	21.7	21.7	20.6	37.1	7

[a] The 6-31G(d) basis set was used in the calculations. [b] The cc-pVTZ basis set was used in the calculations.



Scheme 5 (a) Concerted *vs.* stepwise cycloaddition and (b) concerted fragmentation steps for the global reaction of benzene (**2a**) with tetracyanocarbonyl ylide **1′**.

thiocarbonyl ylides to carbonyl ylides). On the other hand, the only theoretical study on the 1,3-cycloaddition of ozone to benzene was carried out just considering the concerted pathway.[10] Bearing in mind that no previous calculations on tetracyanocarbonyl ylide **1′** have been done to the best of our knowledge, both the concerted and stepwise mechanisms were studied for cycloaddition to the simplest arene (benzene, **2a**) in order to establish the most favorable pathway, if any, that leads to the formation of bicycloadducts. Fig. 1 shows some calculated structures of this reaction step for benzene itself (**2a**), obtained by both the concerted and stepwise mechanisms. As can be seen, there are two possible approaches for **1′** in the concerted pathway, which have been labeled as **ts2** ***endo*** and **ts2** ***exo***. *Endo* approach is that placing the oxygen atom of **1′** above the aromatic ring, whereas in the *exo* approach, the oxygen atom is on the opposite side (Fig. 1). In both cases, the cycloaddition TS are C_s-symmetric and correspond to a synchronous reaction pathway, with C–C bond forming distances almost identical (*ca.* 2.2 Å). The TS are relatively early as indicated by the similar geometric parameters of the TCNEO moiety in the TS with regard to the free reagent **1′**, and also for the relatively small deformation of the aromatic ring. From the energy point of view, the *exo* TS is slightly lower in energy, by *ca.* 0.4 kcal mol^{-1}.

Contrary to that observed for the TS, the cycloadduct **3a** is not symmetric, the cyclohexadiene moiety adopting a half-chair conformation that breaks the C_s symmetry observed along the first part of the reaction coordinate.

The stationary points of the stepwise mechanisms could also be located through the UB3LYP method. The TS for the formation of biradical, namely **ts2a′I**, shows only small deformations of the reactants and a separation of 1.89 Å for the new C–C bond. Its energy is 31.9 kcal mol^{-1} relative to reactants, and demonstrates that the concerted TS is favored by 3.3 kcal mol^{-1}. Rotation about the new bond of the biradical intermediate **3a′I** (73% of biradical character) generated directly from **ts2′I** leads to a slightly lower energy biradical intermediate **3a′II** (99% of biradical character) which adopts a twisted structure. The terminal radical centers are slightly pyramidalized in both intermediates **3a′I** (12.4°) and **3a′II** (5.2°). The energy of formation, *ca.* 29 kcal mol^{-1} confers a great destabilization with respect to the reactants and a highly endergonic character to this first step. Intermediate **3a′II** leads to a very early TS, namely **ts2a′II**, with a small barrier of 3.9 kcal mol^{-1} for ring-closure, with a large C–C distance of 3.37 Å. The same preference for the concerted pathway was obtained when comparing single-point CAS(12,12) energies, with **ts2** ***exo*** being more stable than **ts2a′I** by 12 kcal mol^{-1} (see ESI†).

All these computational results, together with the experimental evidences, confirm that the concerted pathway is preferred over the stepwise one. As a consequence, we decided to extend the theoretical study to the cycloaddition of **1′** to other substituted arenes, and then the fragmentation to arylmalononitriles, in a simplified manner and only under closed-shell conditions (B3LYP) and through concerted pathways.

Cycloaddition of tetracyanocarbonyl ylide (1′) to arenes: reaction barriers

Concerning the substituted benzenes, the number of possible reaction channels is multiplied, due to the presence of the

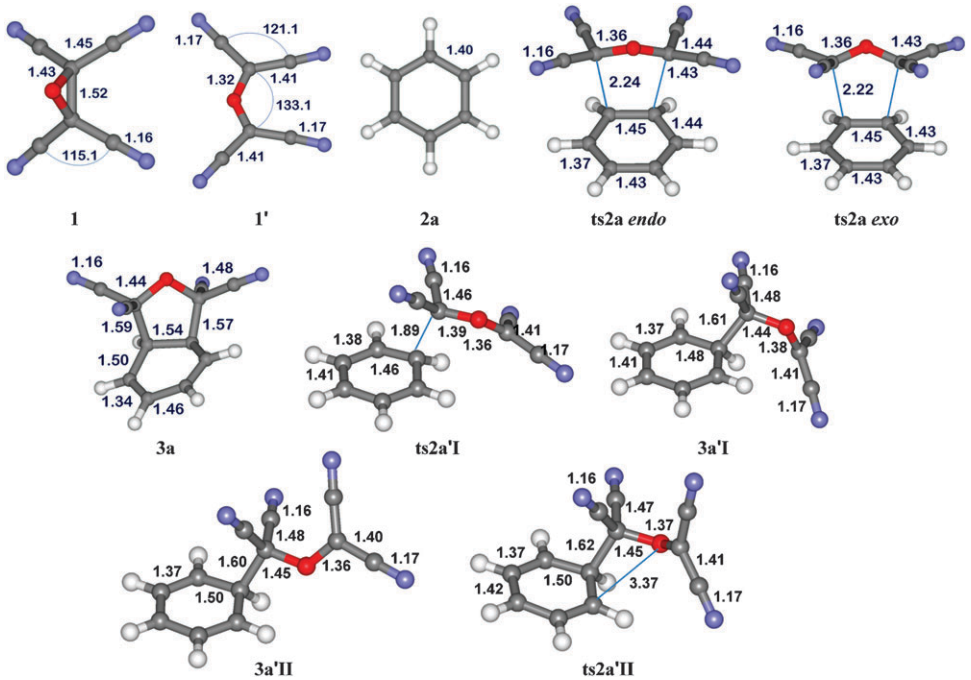


Fig. 1 Calculated structures of the main stationary points of the cycloaddition of TCNEO on benzene through concerted (B3LYP/6-31G(d) level) and stepwise (UB3LYP/6-31G(d) level) pathways. Some relevant geometrical parameters (distances in Å and angles in degrees) are given.

substituent, and thus we have three possible regioisomers, labeled, as a function of the relative position of the benzene substituent and the nearest forming C–C bond, as *ipso*, *ortho* and *meta* TS. Of course, in each case, *endo* and *exo* approaches of **1′** are possible, leading to six possible TS for each cycloaddition reaction. Furthermore, in the case of anisole (**2e**) there are two possible conformations of the methoxy group. Table 2 gathers the calculated relative energies of this cycloaddition step for all the aromatic compounds considered in this work (**2a–f**), taking only the minimum energy value for the stationary points of each of the possible reaction channels (full results are given in ESI†). As can be seen in Table 2, activation barriers increase as the benzene substituent becomes more electron-withdrawing: from 23 kcal mol^{-1} in the case of anisole until 33 kcal mol^{-1} in the case of nitrobenzene. This calculated reactivity is in good agreement with the experimental observations.[7–9] If we plot the relative calculated activation energies against the Brown σ_p^+ (since it is expected that TCNEO carbons reacting with the aromatic compound carry considerable positive charge), a good linear correlation is obtained (Fig. 2), indicating the essentially electronic origin of the relative reactivity. In this sense, nitrobenzene, whose reactivity is diminished by strong inductive effects, should have in contrast a greater capability to delocalize, and thus stabilize, the radical generated in the benzene ring than any other arene in this series. As a result, if the stepwise channel was involved in the reaction, nitrobenzene should react to some extent with TCNEO. Therefore, the experimental results (no reaction with nitrobenzene at all), reinforce the aforementioned preference for the concerted cycloaddition pathway.

Cycloaddition of tetracyanocarbonyl ylide (1′) to arenes: selectivity

The second observation that can be drawn from the results summarized in Table 2 is that *meta* TS are always the lowest

Table 2 Calculated B3LYP/6-31G(d) relative Gibbs free energies (in kcal mol^{-1}) of the reaction intermediates and transition structures of the different reaction channels

	Substituent of the aromatic ring					
	a: H	**b**: Me	**c**: F	**d**: Cl	**e**: OMe	**f**: NO_2
1′ + 2	0.0	0.0	0.0	0.0	0.0	0.0
ts2i	28.0	30.4	31.3	34.5	26.5	35.9
ts2o		27.8	29.6	30.7	24.8	32.6
ts2m		26.9	29.1	30.2	23.4	33.3
3i	−1.0	2.3	2.1	5.7	4.4	11.3
3o		−2.0	1.0	1.2	−4.5	3.0
3m		−2.1	0.2	1.0	−4.2	4.2
ts3p	34.9	32.2	35.1	36.7	27.0	41.4
6p	18.9				14.1	
ts4p	18.8				15.6	
4p + 5	−41.6				−42.0	

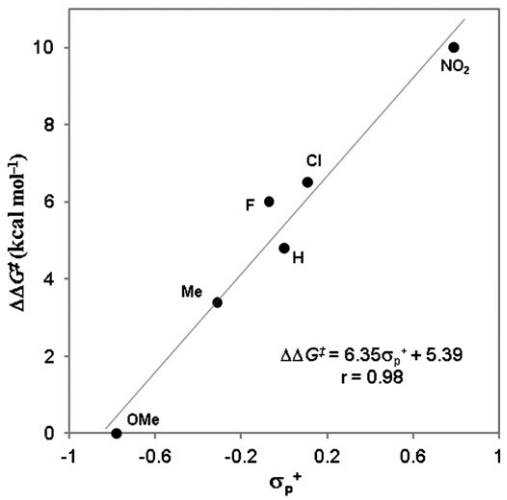


Fig. 2 Plot of calculated relative **ts2m** energies *vs.* Brown σ_p^+.

ones in energy (excepting the case of nitrobenzene, where the *ortho* approach is slightly favored). This observation can also be contrasted with the experimental observations depicted in Scheme 2, bearing in mind that experimental cycloadduct isomer ratios were determined in a very approximate way.[18] In line with the calculated energy barriers, the *meta* adducts are the major products in most cases. For anisole (**2e**), for which only the final *para*-arylmalononitrile was isolated, the *ortho*/*meta* ratio (**3eo**/**3em**) should be very close to zero (see above). This observation agrees quite well with the energy difference between **ts2eo** and **ts2em**, which is the greatest one in the series. For other benzene derivatives (**2b**, **2c**, **2d**) this energy gap is smaller, and therefore the experimental obtaining of a mixture of isomers is justified. Finally, if nitrobenzene (**2f**) was forced to react with TCNEO, it would be expected to obtain a similar proportion of the *ortho* and *meta* adducts, **3fo** and **3fm**. Note that in no case the monoadduct corresponding to the *ipso* attack was experimentally observed, and this corresponds to the TS *ipso* being always higher in energy than the others (by *ca.* 3–4 kcal mol^{-1}).

Cycloreversion from tetrahydroisobenzofurans to arylmalononitriles

Two possible reaction pathways exist from cycloadducts **3**. On the one hand, the retro-cycloaddition reaction can take place, leading to the initial aromatic compound plus TCNEO. On the other hand, the cycloadduct can experience dissociation (also called fragmentation), by losing a molecule of carbonyl dicyanide (**5**), to give a zwitterionic intermediate **6**, which subsequently evolves to the final arylmalononitrile product, **4**. This kind of thermal fragmentation has been previously observed as a secondary process of the cycloaddition of **1** to aryl imines.[19] Scheme 5 shows these two alternative reaction pathways in the case of benzene.

In view of the results obtained in the first part of this work, the loss of **5** was considered to take place only through a concerted TS (**ts3**), which formally correspond to a different retro-cycloaddition. In this case, **5** would act as the dipolarophile and **6** as the dipole. Some selected geometrical features of

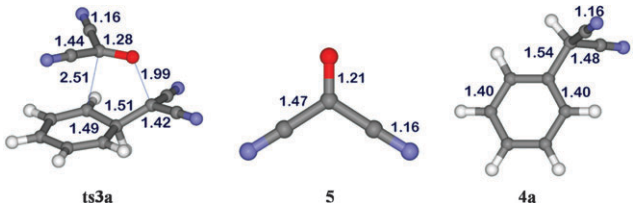


Fig. 3 Calculated (at the B3LYP/6-31G(d) level) structures of the main stationary points of the dissociation of cycloadduct **3a** into carbonyl cyanide (**5**) and phenylmalononitrile (**4a**). Some relevant geometrical parameters (distances in Å and angles in degrees) are given.

this TS in the case of benzene (**ts3a**) are given in Fig. 3. The full mechanism of the global process including the zwitterionic intermediates (**6**) and the aromatization TS (**ts4**) was studied only for benzene and anisole with illustrative purposes. The energies and geometries of these structures can be found in Table 2 and ESI,† although a detailed discussion beyond the reaction barriers of fragmentation (**ts3**) is not relevant in the whole context of this work.

Concerning the reaction energies, it can be seen from values given in Table 2, that the decomposition of **3** to give the arylmalononitrile is favored by electron-donating substituents in the aromatic group, similarly to what happened for the initial cycloaddition. It must be noted that, although all possible fragmentation TS from the corresponding adducts (**ts3o** from **3i**, **ts3m** from **3o** and **ts3p** from **3m**) were calculated (see ESI†), only those leading to the *para* isomers of each arylmalononitrile appear in Table 2 for simplicity. In this case the activation barriers from the *meta* isomers of products **3** are lower, ranging from *ca.* 31 kcal mol^{-1} (**3em** → **ts3ep**) to *ca.* 37 kcal mol^{-1} (**3fm** → **ts3fp**). On the other hand, the activation barriers for the retro-cycloaddition starting from the same adducts **3** are rather insensitive to the substituent in the aromatic ring.

In relation to the alternative reaction pathways, by comparing the activation barriers of Table 2, it can be concluded that the retro-cycloaddition **3m** → **2** + **1′** is systematically favored over the decomposition **3m** → **4p** + **5**, and that the energy difference between both pathways increases as the substituent becomes more electron-withdrawing. However, when the energy of the overall process is taken into account, it can be seen that the formation of **4p** is highly exergonic (*ca.* −41 and −38 kcal mol^{-1} from **3am** and **3em**, respectively, see Table 2), so the formation of the arylmalononitriles from the **3** cycloadducts is thermodynamically favored.

An overview of the global process (starting from tetracyanocarbonyl ylide **1′**) in the case of **2a**, **2e** and **2f**, showing the influence of the substituent on the relative barriers is shown in Fig. 4. It is easy to see that only in the case of anisole (**2e**) the formation of the corresponding arylmalononitrile is highly favored, and furthermore, the relative low and similar activation barriers starting from **3em**, and the relative instability of **3em** with regard to reactants and products explain the difficulty in isolating this adduct. In the case of benzene (**2a**), the second barrier is significantly higher than the first one, so that the cycloadduct **3a** can be isolated, but the final phenylmalononitrile **4a** is still reachable under

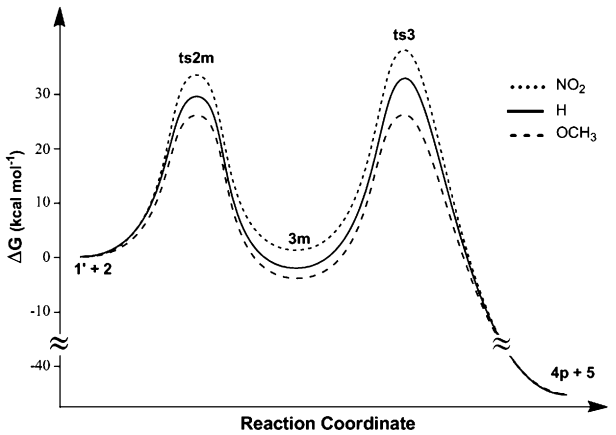


Fig. 4 Calculated relative energies of the different reaction intermediates and transition structures (only the *meta* derivatives are displayed) for the idealized whole pathways of three different aromatics (benzene, anisole and nitrobenzene).

thermodynamic conditions. Finally, in the case of nitrobenzene (**2f**), the high activation barrier of the first step prevents the formation of the cycloadduct **3f** in the same reaction conditions.

Conclusions

The present computational mechanistic study clearly shows that benzene and some of its substituted derivatives are able to react with the open form of TCNEO to give tetrahydroisobenzofurans. The reactivity is highly dependent on the electron-donating character of the benzene substituent. The fate of the cycloadducts also depends on this character. Thus, in some cases, they can be isolated (as in the case of benzene itself), but in other cases, they can evolve by decomposition leading to carbonyl dicyanide and the corresponding arylmalononitrile. When kinetically possible, the latter process is thermodynamically irreversible, constituting a way to obtain these synthetically useful intermediates. It has not escaped to our notice that the reactions here discussed are an alternative to the used methods to prepare arylmalonitriles,[20–24] but this will need to optimize the experimental procedures.

Experimental

Computational methods

All of the geometry optimizations reported in this paper were performed within the density functional theory,[25] using the hybrid three-parameter functional commonly denoted as B3LYP.[26] The standard 6-31G(d) basis set was used for the geometry optimization and the calculation of frequencies.[27] BSSE corrections were not considered in this work. All the stationary points located were characterized by the correct number and nature of their imaginary frequencies. Scaled frequencies were not considered since significant errors in the calculated thermodynamical properties are not found at this theoretical level.[28] The influence of increasing the basis set size was demonstrated to be very small when calculating relative stabilities and relative energy barriers through single-point energy calculations at the B3LYP/6-311 + + G(2d,p) theoretical level[29] (see ESI†). Therefore, unless otherwise stated, B3LYP/6-31G(d) zero-point corrected (for isomers evaluation) and Gibbs free energies (for energy barriers and reactivity studies) were used throughout the discussion. Mass-weighted intrinsic reaction coordinate (IRC) calculations were carried out for the ring-opening of TCNEO and its reaction with benzene (both concerted and stepwise pathways) by using the Gonzalez and Schlegel scheme.[30] In all cases, the Gaussian 03 suite of programs was used.[31] The possibility of different conformations was taken into account for all structures. Both closed-shell (B3LYP) and open-shell (UB3LYP) formulations were employed where necessary, the latter being performed including the keyword guess = mix in Gaussian. The keyword stable = opt was employed to search for an improved UB3LYP wavefunction with a lower total energy when B3LYP and UB3LYP gave identical results, *i.e.* when the biradical character was less than the 30%. Only singlet spin states were considered for all the structures, although non-negligible spin contamination with triplet states is expected on potentially biradical species. As a referee suggested, the triplet energies of these structures were calculated at the same level of theory to better interpret the results for biradical singlet energies. The amount of spin contamination was estimated by checking the expectation value of the S^2 operator, $\langle S^2 \rangle$, after annihilation of the first spin contaminant (triplet) on the converged SCF solution (*i.e.* the energy and the wavefunction were not corrected for spin contamination). The biradical character (BRC) was determined when necessary by single-point CASSCF/6-31G(d) calculations (henceforth CAS) at the UB3LYP/6-31G(d) geometries following the definition of Jensen,[32] that is, the value $[(2 - \mu_H) \times 100]$ where μ_H is the occupation of the HOMO natural orbital. The active space for the CAS calculations was selected by reading the natural orbitals previously generated in the UB3LYP calculations. This strategy very often involved the inclusion of the HOMO and LUMO together with the π and π* orbitals of the cyano groups. The complex electronic structure of reactants forced us to include a high number of electrons and orbitals in the active space, making the most expedient CAS calculations to be nearly impracticable; nevertheless, some benchmarking was done and (6,6) and (12,12) active spaces were selected as adequate approximations for the reactants (tetracyanocarbonyl ylide and benzene) and the stationary points of the benchmark cycloaddition reaction, respectively. Although it was found that the calculated biradical character of a given structure depends on the selected active space, the reported values can be considered a good semi-quantitative estimation.

In spite of its inherent difficulties to correctly describe singlet biradicals due to its single reference character, another highly correlated method like CCSD(T) was used to complement the DFT and CAS results. As previously reported on similar studies,[10] only the inner core electrons were excluded from the correlation treatment through this method. It is assumed that the coupled cluster methods only give highly reliable results with big basis sets, so the more adequate cc-pVTZ basis set was used. The T_1-*diagnostic* defined as the norm of the singles amplitude vector divided by the square root of the number of (correlated) electrons was used as an

internal evaluation of the quality of the CCSD wave function.[33] The size of the structures calculated on the second part of this work (the cycloaddition reaction) made the CCSD(T)/cc-pVTZ methodology to be impractical. Furthermore, the calculation of the CCSD(T) energies of these compounds using a smaller basis set like 6-31G(d) gave unacceptable values of the T_1-*diagnostic* (greater than 0.02). Therefore, the coupled cluster theory could be confidently used only in the study of the activation of TCNEO (**1**). Full details on calculated structures and energies can be found in the ESI.†

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