

Cyanophenylation of Aromatic Nitriles by Terephthalonitrile Dianion: Is the Charge-Transfer Complex a Key Intermediate?^[‡]

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The interaction of terephthalonitrile (**1**) dianion (**1**²⁻) with benzonitrile (**2**) or *m*-tolunitrile (**3**) provides 4,4'-dicyanobiphenyl (**4**) or 4,4'-dicyano-2-methylbiphenyl (**5**), respectively. This result shows that dianion **1**²⁻ serves as a reagent for *p*-cyanophenylation of aromatic nitriles. Based on experimental data, such as the chemical trapping of the 4,4'-dicyanobiphenyl precursor 4-cyano-1-(*p*-cyanophenyl)cyclohexa-2,5-dienyl anion (**7**) and the failure to obtain biphenyl **4** through the interaction of independently generated radical anions (RAs) **1**^{•-} and **2**^{•-}, as well as on the results of quantum-chemical calculations, a mechanism is suggested that includes a charge-transfer complex (CTC) between **1**²⁻ and the aromatic nitrile as the key intermediate. The formation of this CTC is

followed either by an intracomplex electron transfer (ET) and recombination of terephthalonitrile and aromatic nitrile RAs within an unequilibrated RA pair, or by synchronous ET and bonding of the *ipso*-carbon atom of terephthalonitrile with the *p*-carbon atom of the aromatic nitrile. The synthetic significance of *p*-cyanophenylation of arenecarbonitriles by dianion **1**²⁻ is illustrated by the high yield of biphenyl product **4** (approx. 90 %) as well as by the possibility of a one-pot synthesis of 4-butyl-4'-cyanobiphenyl and 4-butyl-4'-cyano-2-methylbiphenyl by successive treatment of dianion **1**²⁻ with nitrile **2** or **3** and butyl bromide.

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Introduction

Conversion of aromatic compounds into their anionic reduced forms by means of one- or two-electron reduction has proved to be a fruitful approach to their activation toward interaction with electrophiles, most commonly with alkyl or acyl halides and anhydrides of carbon acids.^[1–8] The utilisation of functionalised arenes as electrophiles in reactions with these anionic reduced forms is still extremely scarce. As a rule, it concerns aryl halides, which undergo reductive dehalogenation while reacting with the arene anionic reduced form.^[1] However, there are few examples of bond formation between the neutral and reduced arenes during their interaction, either when the arene radical anion (RA) combines with its neutral precursor or when the reduced arene serves as an arylating reagent for neutral arenes of different structural types.^[9] The latter case is of special synthetic value; for instance, quinoline,^[9a] pyridine^[9b] or 2-methylpyridine^[9c] *N*-oxides react with ketyl and the dianion of benzophenone to form *N*-oxide diphenyloxymethyl de-

rivatives. Also, the 2,3'-biquinolyl dianion is arylated with aryl and heteroaryl halides.^[10]

Previously we have shown that RAs, especially cyanocyclohexadienyl anions and dianions generated by reduction of aromatic nitriles with an alkali metal in liquid ammonia, are quite stable in the absence of oxygen and moisture. These anionic reduced forms have been successfully used as highly reactive reagents for arylation of alkyl halides, providing good yields of alkylarenes or alkylcyanoarenes.^[11–21] In particular, the synthesis of *p*-alkylbenzonitriles by the interaction of two-electron-reduced terephthalonitrile, dianion **1**²⁻,^[20] with various alkyl halides has been developed.^[22] With the aim of developing a general synthetic methodology based on reductive activation of aromatic nitriles and utilisation of their anionic reduced forms as versatile cyanoaryllating reagents, it is worthwhile to extend the structural diversity of the electrophilic substrate, particularly on aromatic compounds. The present article is devoted to the investigation of the interaction of **1**²⁻ with the aromatic nitriles benzonitrile (**2**) and *m*-tolunitrile (**3**).

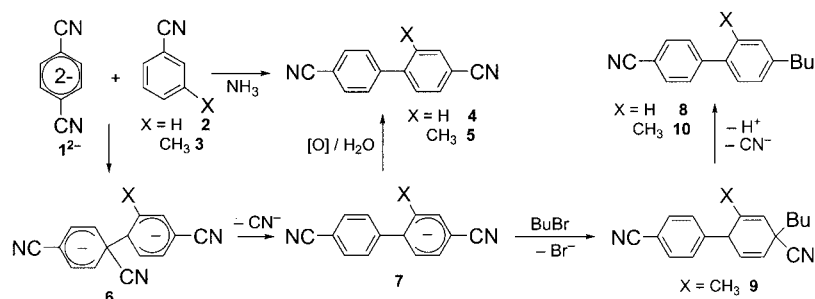
Results and Discussion

As reported earlier,^[20] **1**²⁻ was generated by the addition of two equivalents of alkali metal (Na, K) to a suspension of dinitrile **1** in liquid ammonia under inert atmosphere (argon or ammonia). The interaction of the thus-obtained salt of **1**²⁻ with nitrile **2** results in the formation of 4,4'-dicya-

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Scheme 1.

Table 1. The reaction of dianion 1^{2-} with nitriles **2** and **3** in liquid ammonia.

Entry	Amount of reagents [mmol] 1	Alkali metal	Nitrile	1^{2-} conc. [mol L ⁻¹]	Temp. [°C]	Time [h]	Product weight [g]	Product composition [mmol] (mol-%) ^[a,b] 1 2, 3 Biphenyls			
1	5.0	K 10.0	2 5.0	0.1	-33	1	1.03	0.4 (7)	2 3.2	4 3.2 (64)	
2 ^[c]	5.0	K 10.0	2 5.0	0.1	-40 to -45	6	1.02		2 3.7	4 3.0 (60)	
3	2.5	Na 5.0	2 2.5	0.08	-33	1	0.45	0.8 (32)	2 1.2	4 1.1 (45)	
4 ^[c]	2.5	Na 5.0	2 2.5	0.08	-75	1	0.36	0.7 (28)	2 1.0	4 0.5 (20)	
5 ^[c]	5.0	Na 10.0	2 5.0	0.1	-70 to -78	4	0.87	0.5 (10)	2 2.8	4 0.8 (16)	
6	2.5	Na 5.1	2 5.2	0.06	-33	1	0.66	0.2 (8)	2 2.8	4 1.7 (68)	
7	2.5	Na 5.0	2 10.0	0.06	-50	3	1.08	0.1 (4)	2 6.6	4 1.9 (76)	
8	15.0	Na 31.0	2 18	0.5	-33	1	3.11	0.4 (3)	2 5.9	4 12 (80)	
9	25.0	Na 51.0	2 51	0.5	-33	1	6.8		2 20	4 23 (92)	
10	5.0	K 10.0	3 5.0	0.1	-33	1.2	0.90	0.3 (6)	3 2.8 2 2.1	5 1.2 (24) 4 0.2 (4)	
11	5.0	Na 10.0	3 5.0	0.15	-33	0.9	0.70	0.2 (4)	3 0.3 2 0.1	5 2.2 (44) 4 0.7 (14)	

[a] Calculated as mean values of no less than three runs. Deviation does not exceed 5%. [b] During the experimental procedure the volatile nitriles **2** and **3** partially (up to 30%) evaporated off with the ammonia. An additional amount of nitrile **2** can be formed due to protonation^[20,23,24] of dianion 1^{2-} during the reaction course or its treatment. [c] Besides compounds included in the table, the reaction mixtures also contained *p*-cyanobenzamide, which results from partial hydrolysis of dinitrile **1** [entry 2: 0.2 mmol (4%); entry 4: 0.4 mmol (16%); entry 5: 2.4 mmol (48%)].

nobiphenyl **4** (see Scheme 1). The yield of **4** varies from 16 to 90% depending on the reaction conditions (see entries 1–9, Table 1): an increase of the reaction temperature (entries 3–5) and an increase of the amount of **2** (entries 3, 6 and 7) and of the reagents' concentration (entries 3, 8 and 9) increase the yield of the biphenyl product.

On the addition of nitrile **3** to a suspension of 1^{2-} salt in liquid ammonia *p*-cyanophenylation also takes place to give 4,4'-dicyano-2-methylbiphenyl (**5**; see entries 10 and 11 in Table 1, and Scheme 1). No spectroscopic data for biphenyl **5** could be found in the literature. Its structure was confirmed by ¹H NMR and IR spectroscopy and HR mass spectrometry (see Experimental Section). The substituent positions in the biphenyl framework are indicated by the presence of the following signals in the ¹H NMR spectrum: an AB pattern at δ = 7.62 and 7.91 ppm (J_{ortho} = 8 Hz) due to the protons H^{2'}, H^{6'} and H^{3'}, H^{5'} of the *p*-disubstituted ring, the doublet at δ = 7.46 ppm (J_{ortho} = 7.5 Hz), attributed to H⁶, the low-field-shifted doublet of doublets at δ = 7.71 ppm (J_{ortho} = 7.5, J_{meta} = 1.5 Hz), and the doublet at δ = 7.75 ppm (J_{meta} = 1.5 Hz) belonging, respectively, to H⁵ and H³ *ortho* to the cyano group.

The formation of **5** as the main product of the reaction of dianion 1^{2-} and nitrile **3** testifies that the aromatic frag-

ments in the biphenyl product come from different reaction participants. The presence of a small amount of biphenyl **4** among the products is most probably caused by the interaction of 1^{2-} with **2**, which could be formed by the protonation of 1^{2-} by entrapped moisture^[20,23,24] or by nitrile **3** itself.^[25]

Thus, the results obtained show that the dianion 1^{2-} is the reagent of choice for *p*-cyanophenylation of aromatic nitriles. The intermediate formation of biscyclohexadienyl dianion **6**, followed by rapid cyanide-ion elimination resulting in the relatively stable phenylcyclohexadienyl anion **7** (see Scheme 1), is highly probable. The contact of the latter with air leads to the biphenyls **4** and **5**. The reality of the suggested reaction course is proved by the following experimental facts: cyclohexadienyl anions containing, like the dianion **6**, a cyano group and hydrogen atom^[23,24] or alkyl group^[19,20] in geminal positions undergo rapid aromatisation due to decyanation, whereas cyclohexadienyl anions like **7**, without a good leaving group at the saturated carbon atom, are quite stable under the given experimental conditions.^[19,26]

That anion **7** is a relatively stable reaction intermediate is confirmed by the formation of 4-butyl-4'-cyanobiphenyl (**8**) or two other "butoxided" products – 4-butyl-4-cyano-

1-(*p*-cyanophenyl)-2-methylcyclohexa-2,5-diene (**9**) and 4-butyl-4'-cyano-2-methylbiphenyl (**10**) – when butyl bromide was added to the reaction mixture of **1**²⁻ and nitriles **2** or **3** before allowing it to come into contact with the air (see Scheme 1). Besides the main compounds **8**–**10**, the product mixtures also contained components formed by the butylation of dianion **1**²⁻ and RA **1**¹⁻ (*p*-butylbenzonitrile^[18,20] and the anionic reduced forms of nitriles **2** or **3** (butylarenes and butyldihydroarenes^[11,16a] respectively). Butylbiphenyl **8** has been described previously,^[27,28] while no information about products **9** and **10** was found. Diene **9** was formed and isolated as a mixture of nearly equal amounts of *cis*- and *trans*-isomers. The signals in the ¹H NMR spectrum of **9** (see Experimental Section) were attributed on the basis of a comparison with the spectrum of cyclohexadienyl products formed by the alkylation of anionic reduced forms of *m*- and *p*-tolunitriles.^[16a,16b] Assignment of the signals in the ¹H NMR spectrum of **10** was similar to that described above for the biphenyl **5**.

It is obvious that the key to understanding the mechanism of *p*-cyanophenylation of cyanoarenes by dianion **1**²⁻ is the answer to the question of how the dimeric dianion **6** is formed. In this connection it is important to determine whether the *p*-orientation is typical for the reactions of cyanoarenes with carbanionic reagents in liquid ammonia or not. We have shown that the cyanomethyl anion, generated from acetonitrile by treatment with sodium amide in liquid ammonia and which, to some extent, models the fragment of dianion **1**²⁻ that bears the main part of the negative charge (compare with the charge distribution in the dianion of 9-cyanoanthracene^[26]), reacts with **2** to give β-aminocin-namonitrile (**11**).^[29,30] This result shows that the carbanion adds to the cyano group of **2** and suggests that the interaction of dianion **1**²⁻ with an aromatic nitrile proceeds through a mechanism that is different from that typical for α-cyano-substituted carbanions (see Scheme 2). On this basis, while considering the mechanism of the interaction of dianion **1**²⁻ with aromatic nitriles within the dichotomy between straight nucleophilic attack, on the one hand, and electron transfer (ET), on the other, the latter seems preferable. There are at least two reasons for that. Firstly, the correlation of reduction potentials of **1** and **2** ($E^0_{1/1^-} = 1.25$, $E^0_{2/2^-} = 1.99$, $E^0_{1^-/1^{2-}} = 2.20$ V, AgCl/DMF/TMACl^[24]) makes ET from **1**²⁻ to **2** exothermic. Additionally, the calcu-

lated (RHF/6-31+G*, see Figure 1) HOMO energy level of dianion **1**²⁻ is significantly higher than the levels of both LUMO (*b*₁) and even next vacant MO (*a*₂) of nitrile **2**. Thus, the possibility of ET from the dianion HOMO (*b*_{1u}) to both *b*₁ and *a*₂ MOs of the mononitrile should be taken into account. The total energies (*E*_{tot}) of **1**²⁻ and **2** as well as **1**¹⁻ and **2**¹⁻ (Table 2), together with the energy changes (*E*_{rel}) due to the ET (Table 3), show the thermodynamic possibilities of all the above-mentioned variants of ET. This implies that the RA pair could appear not only in the ground but also in an excited electronic state.

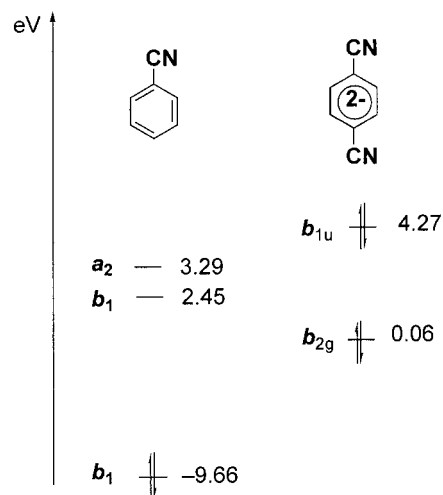
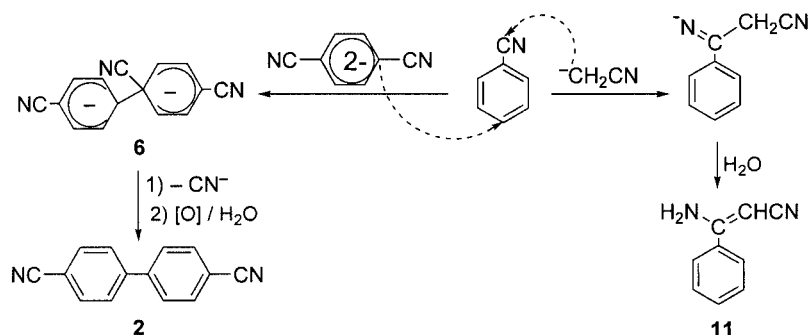


Figure 1. The diagram of dianion **1**²⁻ and nitrile **2** boundary MO energies (RHF/6-31+G*).

Secondly, incorporation of the cyanophenyl fragment into the nitrile moiety at the *para* position is the regioselectivity typical for the recombination of aromatic nitrile RAs^[31–34] because of the maximum spin-density localisation in the *para* position of the nitrile RA.^[35,36] Small amounts of compounds formed by butylation of RAs **1**¹⁻, **2**¹⁻ and **3**¹⁻ found among the products of those experiments when dianion **1**²⁻ was successively treated with aromatic nitrile and butyl bromide also testify, to a certain extent, in favour of an ET mechanism.



Scheme 2.

Table 2. Results of the HF/6-31+G* and MP2/6-31+G*//HF/6-31+G* calculations on dianion 1^{2-} , nitrile **2**, and their vertical RA states 1^{-} and 2^{-} .^[a]

System (state)	Electron configuration	E_{tot} [a.u.]	
		HF	MP2
1^{2-} ($^1A_{1g}$)	$\dots(b_{2g})^2(b_{1u})^2$	-414.013856	-415.369547
1^{-} ($^2B_{1u}$)	$\dots(b_{2g})^2(b_{1u})^1$	-414.171698	-415.519347
2^0 (1A_1)	$\dots(a_2)^2$	-322.447642	-323.484440
2^{-} (2B_1)	$\dots(a_2)^2(b_1)^1$	-322.398775	-323.455423
2^{-} (2A_2)	$\dots(a_2)^2(b_1)^0(a_2)^1$	-322.376229	–

[a] The RA states were calculated by the ROHF/6-31+G* method with the geometry of the respective closed-shell systems.

Table 3. Relative energies of initial and resulting states of vertical ET between dianion 1^{2-} and nitrile **2** from the data in Table 2.

Pair of isolated particles		E_{rel} [kcal mol ⁻¹]	
		HF ^[a]	MP2
1^{2-} ($^1A_{1g}$)	2^0 (1A_1)	0	0
1^{-} ($^2B_{1u}$)	2^{-} (2B_1)	-68.4	-75.8
1^{-} ($^2B_{1u}$)	2^{-} (2A_2)	-64.4	–

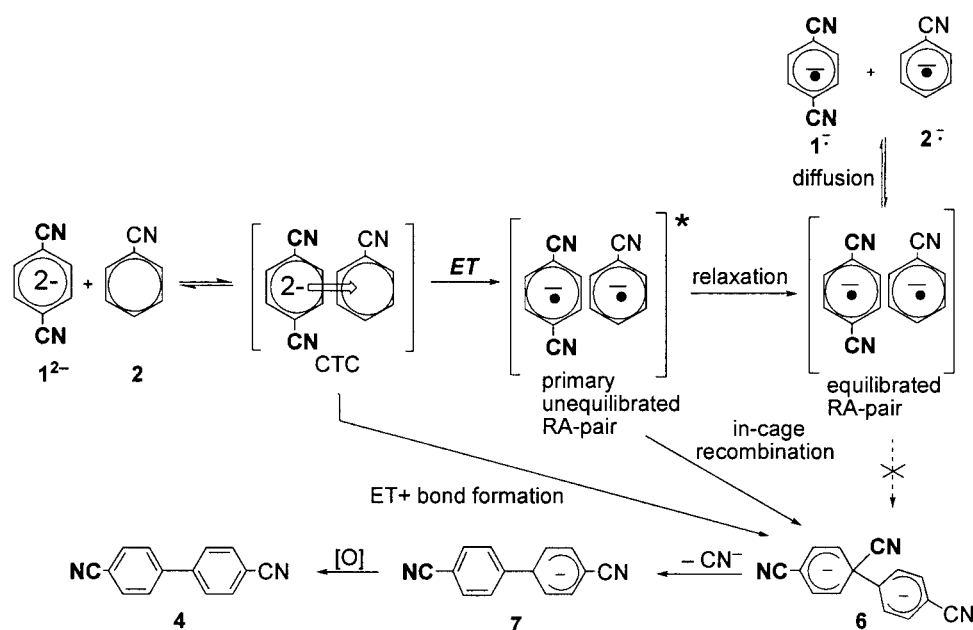
[a] See footnote to Table 2.

In light of these considerations it is necessary to examine the possibility of biphenyl formation by the diffusional recombination of independently generated 1^{-} and 2^{-} . It is well known that 1^{-} generated electrochemically^[23,24] or by the action of alkali metal in liquid ammonia^[18] doesn't undergo self-recombination. Dimerisation of RA 2^{-} has proved to be reversible^[31,32] and, when generated in liquid ammonia, this RA doesn't yield dimeric products,^[11] particularly biphenyl **4**. These data, along with the origin of the phenyl moieties in the biphenyl product from different reaction participants, allow us to exclude self-recombination of RAs as the main route of biphenyl formation. Nevertheless, the possibility of diffusional cross-recombination

of RAs 1^{-} and 2^{-} cannot be excluded due to the rapid irreversible decyanation of the initially formed dimeric dianion **6** to provide monoanion **7**. We tried to realise cross-recombination of 1^{-} and 2^{-} in two ways: solutions of RAs prepared by the reduction of each nitrile (**1** or **2**) by sodium in liquid ammonia were mixed, or one equivalent of dinitrile **1** was added to a solution of two equivalents of RA 2^{-} . The reduction potentials of nitriles **1** and **2** given above indicate that 2^{-} should reduce dinitrile **1** to 1^{-} . In both cases no traces of biphenyl **4** were observed among the products formed after oxidation of the reaction mixtures by atmospheric oxygen. Treatment of the mixture prepared in the second case with butyl bromide resulted in the formation of the butylation products of both 1^{-} (*p*-butylbenzonitrile and 2-butyl-1,4-dicyanbenzene^[18]) and 2^{-} (butylbenzene and 1-cyano-1-butylcyclohexa-2,5-diene^[11]). No biphenyl products were formed. These results suggest that in the course of the reaction between dianion 1^{2-} and nitrile **2** the dimeric dianion **6** cannot be a product of diffusional cross-recombination of 1^{-} and 2^{-} , and must thus be formed by some other pathway.

All the above results induced us to consider a mechanism involving the charge-transfer complex (CTC) as a key intermediate formed in a reaction stage preceding ET.^[37] This mechanism is the equivalent of an inner-sphere ET.^[38] Applying the main ideas of this approach to the reaction under investigation, it is necessary to suppose the formation of a CTC between dianion 1^{2-} as a donor and nitrile **2** as acceptor, followed by an adiabatic ET (see Scheme 3).

In accordance with this concept we performed single-point MP2/6-31+G* calculations to test the expected character of the total energy changes of 1^{2-} and **2** under their plane-parallel and coaxial approach with mutual rotational orientation, which ensures maximal proximity of the bond-forming positions when the CTC transforms into dianion



Scheme 3.

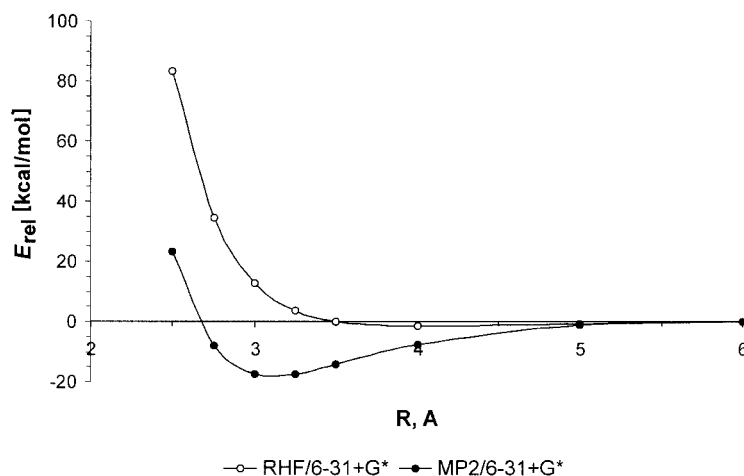


Figure 2. Energy changes at the plane-parallel and coaxial approaches of dianion **1**²⁻ and mononitrile **2** (RHF/6-31+G* and MP2/6-31+G*).

6 (“eclipsed” conformation^[39,40]). The fragments’ geometry was found to be invariable. These results demonstrate that the system of **1**²⁻ and **2** stabilizes under approach of its components to each other and reaches an energy minimum at a distance between the ring planes, R_{eq} , of about 3.15 Å (Figure 2). This finding entirely complies with the CTC formation so far, as typical stacking distances in CTCs formed by radical cation^[37b] or RA^[41,42] and the neutral precursor molecule lie in the range 2.9–3.6 Å. It is worthwhile to note that the orientation indicated above is not necessarily optimal. Thus, rotation of one of the CTC fragments by 90° whilst retaining the coaxial arrangement of the rings (“staggered” conformation) leads to an additional energy reduction of 3.4 kcal mol⁻¹, obviously due to a moving apart of the fragments bearing the principal parts of the negative charge. However, even if the “staggered” conformation is more stable than the “eclipsed” one, there are no reasons to anticipate obstacles preventing interconversion of these two conformations by means of free rotation.

Comparison of the results of the RHF and MP2 calculations (see Figure 2) shows that the existence of the CTC is almost completely due to electron correlation effects. The population analysis within the Löwdin scheme characterises the CTC by a substantial degree of charge transfer from **1**²⁻ to **2** (0.582 according to MP2 calculations). This value is caused by considerable mixing of the MOs of the CTC participants when the intermolecular distance reaches R_{eq} . Thus, the CTC HOMO is mainly the b_{1u} HOMO of dianion **1**²⁻, with a small “admixture” of the b_1 LUMO of nitrile **2** (Figure 3), which, in turn, contributes predominantly to the CTC LUMO. The lowest excited state of the CTC corresponds to electron transfer between its components.

According to the CISD/6-31 calculations in restricted active space, including the π -orbitals of CTC components, the energy of the Frank–Condon ET in the CTC with the formation of RAs **1**⁻ to **2**⁻, separated by R_{eq} , is about 60 kcal mol⁻¹. Although the real endothermicity of this vertical conversion could be markedly lowered by solvation and association with a counterion, it hardly occurs in the dark.

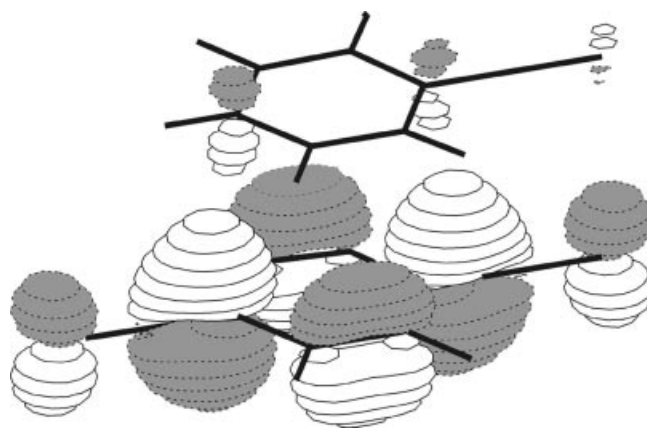


Figure 3. HOMO view of the CTC.

The electron transfer in the CTC is most probably accomplished adiabatically. Two main factors may be significant for tuning the system coordinates that are necessary for the reaction course. The first one implies a certain increase in distance between the ring planes, with a concomitant decrease in the energy gap between the ground and excited states of CTC to a value that allows a thermal ET to occur. The pair of **1**⁻ and **2**⁻ thus formed differs from the “vertical” one by a larger separation of the RAs.^[43] At the same time, in contrast to a diffusion encounter the distance between the RAs, and their reciprocal orientation, could be favourable for recombination to give dimer **6** (see Scheme 3). The second factor is the easy accessibility of the “eclipsed” conformation, which ensure closeness of the **1**²⁻ *i*- and **2** *p*-carbon atoms necessary for bond formation to provide dianion **6**. This process could proceed synchronously with ET and, in such a way, compensate the energy consumption somewhat. The recombination of RAs resulting from the intracomplex ET and therefore closely brought together as well as synchronous ET-recombination process seem to be electrostatically favourable. The reason for this lies in the fact that in going from the CTC to di-

anion **6** the negative charges concentrate predominantly at cyano groups (compare ref.^[26]) moving away from each other.

The scheme proposed for the reaction under investigation to some extent resembles the dynamics of ion pairs formed upon electron-transfer quenching of perylene by tetracyanoethylene, which is defined by ultrafast recombination within the primary quenching product – a contact ion-pair formed in an electronically excited state.^[44] It was found that a rise of quencher concentration results in an increase of the recombination product yield. As applied to the interaction of **1**²⁻ with nitriles **2** or **3**, this finding means that the yield of biphenyls **4** or **5** must increase with the mononitrile concentration. The experimental data agree with this assumption (see entries 3, 8 and 9–11 in Table 1).

It's worthwhile to point out the synthetic significance of this *p*-cyanophenylation of arenecarbonitriles **2** and **3** by terephthalonitrile dianion. The yield of biphenyl **4** in this reaction reaches 92% (see Table 1, entry 10). The methods for the synthesis of compound **4** previously described in the literature involve either a bisaryl condensation catalysed by complexes of Ni^[45] and Pd^[46] or oxidative condensation of the corresponding organomagnesium derivative.^[47] All those approaches utilize less accessible precursors and more complicated experimental techniques and provide lower yields (up to 80%) than the method described in the present article. The scope of aromatic substrates suitable for *p*-cyanophenylation by dianion **1**²⁻ is currently under investigation. Our preliminary results show that 1-naphthonitrile and 9-cyanoanthracene also undergo this reaction. Also, the possibility of a one-pot synthesis of 4-alkyl-4'-cyanobiphenyl by successive treatment of dianion **1**²⁻ with aromatic nitrile and alkyl halide has potential synthetic merit. These compounds are well known and are widely used as liquid crystals components. All previously described methods of their synthesis^[27,28,48] are multi-stage and provide low total yields.

Experimental Section

The ¹H NMR spectra were recorded with a Bruker WP-200 instrument for solutions in [D₆]acetone (concentration 10–15%). The IR spectra were recorded on a UR-20 instrument for samples pelleted with KBr (0.25%) or as thin films. The reaction mixtures were analysed by GCMS on a Hewlett–Packard G1081A instrument consisting of an HP-5890 Series II gas chromatograph and an HP-5971 mass-selective detector (IE, 70 eV) with an HP5 capillary column (30000 × 0.25) mm × 0.25 μm. A He flow (1 mL min⁻¹) was used as carrier gas. The following temperature regime program was applied: 2 min at 50 °C, 50 °C to 280 °C at a rate of 10 °C min⁻¹, 5 min at 280 °C. The evaporator temperature was 280 °C and the ion source temperature 173 °C. The scanning velocity was 1.2 scans per second in the mass interval 30–650 amu. The precise molecular ion weights were determined with a Finnigan MAT-8200 high-resolution mass spectrometer.

Quantum-chemical calculations were performed using the GAMESS package.^[49] The geometry optimisation of dianion **1**²⁻ and nitrile **2** was made in frames with the RHF/6-31+G* method, the geometry changes upon approach of these particles during the

CTC formation was neglected. Electronic correlation was considered at the level of single point MP2/6-31+G**/RHF/6-31+G* calculations. The excitation energies in the CTC were estimated by the CISD/6-31+G* method in restricted active space constructed from all π -orbitals of the fragments. The calculations of RAs **1**⁻ and **2**⁻ were performed using the geometry of the corresponding particles with closed electronic shell in frames of the spin-restricted ROHF/6-31+G* method; the excited states were obtained by vectors permutation in the initial guess. The calculations of the ground states of the RAs were made by the spin-restricted MP2/6-31+G* method.

Starting Materials: Liquid ammonia was purified just before use by dissolving metallic sodium in it, followed by distillation into a reaction vessel cooled to between –80 and –70 °C. Metallic potassium and sodium were freed from their oxide film under dry hexane. Commercial terephthalonitrile (**1**) was purified by sublimation and dried over P₂O₅ in vacuo (m.p. 222 °C; 222–223 °C^[50]). Commercial benzonitrile was distilled from over P₂O₅ just before use. Commercial *m*-tolunitrile was purified by distillation [b.p. 57–58 °C/3 mm (84 °C/10 mm^[51])]. Commercial butyl bromide and acetonitrile were purified by passing through a layer of aluminium oxide, followed by distillation.

Generation of Terephthalonitrile Dianion **1²⁻:** The alkali metal (see Table 1 for the reagent amounts) was added to a stirred suspension of dinitrile **1** in liquid ammonia at –33 °C under argon or evaporating ammonia atmosphere. The mixture was kept for 5 min under the same conditions. The resulting dark-brown suspension of the dianion **1**²⁻ salt was used in further experiments.

General Procedure for Treatment of Dianion **1²⁻ with Aromatic Nitrile:** The desired amount of benzonitrile (**2**) or *m*-tolunitrile (**3**; see Table 1) was added dropwise to a stirred suspension of **1**²⁻ salt, and the reaction mixture was stirred for the required time. Then, the ammonia was evaporated by half, diethyl ether (approx. 50 mL) was added and the reaction mixture was put into contact with air. Stirring was continued until the ammonia had evaporated completely and room temperature reached. Water (approx. 50 mL) was poured onto the residue to dissolve the inorganic salts. The solid organic products were filtered off, washed with diethyl ether and water, dried in air and analysed. The products from the liquid fraction were extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried with MgSO₄, filtered and the solvent was removed. The crude residue was analysed by ¹H NMR spectroscopy and GCMS. The pure products were isolated by TLC on plates with a fixed layer of silica gel (40/70 μm, containing 12 wt.-% of mineral white) and a hexane/diethyl ether mixture (9–8:1 volume ratio) as eluent. The separation was monitored by irradiating the plate with UV light. The fractions were washed with diethyl ether. The structure of the individual products was confirmed by ¹H NMR and IR spectroscopy and HR mass spectrometry.

4,4'-Dicyanobiphenyl (4**):** Metallic sodium (1.18 g, 51.0 mmol) was added in five portions to a suspension of dinitrile **1** (3.20 g, 25.0 mmol) in liquid ammonia (50 mL) at –50 °C (see entry 9, Table 1). The suspension of dianion **1**²⁻ salt thus formed was stirred for 10 min to reach a temperature of –33 °C and nitrile **2** (5.3 mL, 51 mmol) was added dropwise. The reaction mixture was stirred for one hour at the same temperature and treated as described above in the general procedure. The resultant light-ivory powder was identified as biphenyl **4** (4.3 g, 21 mmol), m.p. 237–239 °C (235–238 °C^[52]). The extracted residue (2.5 g) consisted of nitrile **2** (20 mmol) and biphenyl **4** (2.0 mmol). Total yield of **4**: 23 mmol (92%).

4,4'-Dicyano-2-methylbiphenyl (5): Part of the reaction mixture (0.39 g) resulting from the reaction of dianion **1**²⁻ with nitrile **3** (see entry 11, Table 1) was separated by TLC. Biphenyl **5** (0.2 g, 0.9 mmol) was obtained ($R_f = 0.2$) as a white solid, m.p. 168–170 °C. ¹H NMR: $\delta = 2.32$ (s, 3 H, CH₃), 7.46 (d, $J_{5,6} = 7.5$ Hz, 1 H, 6-H), 7.62 (d, $J_{ortho} = 8.0$ Hz, 2 H, 2'-H and 6'-H), 7.71 (dd, $J_{5,6} = 7.5$, $J_{5,3} = 1.5$ Hz, 1 H, 5-H), 7.75 (d, $J_{3,5} = 1.5$ Hz, 1 H, 3-H), 7.91 (d, $J_{ortho} = 8.0$ Hz, 2 H, 3'-H and 5'-H) ppm. IR: $\tilde{\nu} = 2226$ cm⁻¹ (C≡N). HRMS: calculated for C₁₅H₁₀N₂ [M⁺] 218.08449; found 218.08434.

4-Butyl-4'-cyanobiphenyl (8): a) Benzonitrile (0.52 mL, 5 mmol) was added to a suspension of dianion **1**²⁻ salt prepared by the action of metallic potassium (0.39 g, 10 mmol) on dinitrile **1** (0.64 g, 5 mmol) in liquid ammonia (50 mL). The reaction mixture was stirred for 50 min, then butyl bromide (0.53 mL, 5 mmol) was added and stirring was continued for a further 50 min. Subsequent treatment was performed as described above. The product mixture thus obtained (1.05 g) consisted of dinitrile **1** (1.6 mmol, 32%), nitrile **2** (2.5 mmol), 1-butyl-1-cyanocyclohexa-2,5-diene (0.14 mmol, 3% relative to dinitrile **1**), *p*-butylbenzonitrile (0.5 mmol, 10%), biphenyl **4** (0.4 mmol, 8%) and 4-butyl-4'-cyanobiphenyl (**8**; 1.5 mmol, 30%). The latter was obtained as a light-yellow oil (0.04 g, 0.16 mmol) by TLC of part (0.11 g) of the reaction mixture. ¹H NMR: $\delta = 0.92$ (t, 3 H, CH₃), 1.36 (m, 2 H, -CH₂-), 1.62 (m, 2 H, -CH₂-), 2.66 (t, 2 H, -CH₂-), 7.34 (d, $J_{ortho} = 9.0$ Hz, 2 H, 3-H and 5-H), 7.63 (d, $J_{ortho} = 9.0$ Hz, 2 H, 2-H and 6-H), 7.82 (s, 4 H, 2'-H, 3'-H, 5'-H and 6'-H) ppm. IR: $\tilde{\nu} = 2225$ cm⁻¹ (C≡N). HRMS: calculated for C₁₇H₁₇N [M⁺] 235.13609; found 235.13620.

b) Benzonitrile (2.32 mL, 22.5 mmol) was added to a suspension of dianion **1**²⁻ salt prepared by the action of metallic sodium (0.71 g, 31 mmol) on dinitrile **1** (1.92 g, 15 mmol) in liquid ammonia (50 mL). The reaction mixture was stirred for 30 min, then butyl bromide (1.90 mL, 18 mmol) was added and stirring was continued for 1.5 h. Further treatment was performed as described above. The product mixture thus obtained (4.35 g) consisted of dinitrile **1** (2.8 mmol, 19%), nitrile **2** (11 mmol), butylbenzene (1.3 mmol, 9% relative to dinitrile **1**), *p*-butylbenzonitrile (1.2 mmol, 8%), biphenyl **4** (2.3 mmol, 15%) and 4-butyl-4'-cyanobiphenyl (**8**; 8.4 mmol, 56%).

4-Butyl-4-cyano-1-(*p*-cyanophenyl)-2-methylcyclohexa-2,5-diene (9) and 4-Butyl-4'-cyano-2-methylbiphenyl (10): Tolunitrile **3** (0.29 mL, 2.5 mmol) was added to a suspension of dianion **1**²⁻ salt prepared by the action of metallic sodium (0.115 g, 5 mmol) on dinitrile **1** (0.32 g, 2.5 mmol) in liquid ammonia (30 mL). The reaction mixture was stirred for 1 h, then butyl bromide (0.26 mL, 2.5 mmol) was added and stirring was continued for 1 h 15 min. Further treatment was performed as described above. The product mixture thus obtained (0.59 g) consisted of dinitrile **1** (0.20 mmol, 8%), nitrile **3** (0.50 mmol, 20%), 1-butyl-1-cyano-3-methylcyclohexa-2,5-diene (0.16 mmol, 6% relative to dinitrile **1**), *m*-butyltoluene (0.1 mmol, 4% relative to dinitrile **1**), *p*-butylbenzonitrile (0.19 mmol, 8%), biphenyl **4** (0.04 mmol, 2%), 4-butyl-4'-cyanobiphenyl **8** (0.08 mmol, 3%), 4-butyl-4-cyano-1-(*p*-cyanophenyl)-2-methylcyclohexa-2,5-diene (**9**) as a mixture of nearly equal amounts of two isomers (total content 0.43 mmol, 17%) and 4-butyl-4'-cyano-2-methylbiphenyl (**10**; 0.87 mmol, 35%). Part of the reaction mixture (0.334 g) was separated by TLC to give **9** (0.062 g, 0.22 mmol) as a white solid (a mixture of two isomers; $R_f = 0.1$, m.p. 86–89 °C) and **10** (0.115 g, 0.22 mmol) as a sticky light-yellow oil ($R_f = 0.6$).

9: ¹H NMR: $\delta = 0.91$ (t, 3 H, CH₃), 1.38 (m, 4 H, 2 CH₂), 1.59 (s, 3 H, CH₃), 1.82 (m, 2 H, CH₂), 4.00 (m, 1 H, 1-H), 5.66 (m, 1 H, 3-H), 5.83 (dd, $J_{5,6} = 9.0$, $J_{5,1} = 2.5$ Hz, 1-H, 5-H), 5.98 (dd, $J_{6,5} =$

9.0, $J_{6,1} = 4.0$ z, 1 H, 6-H), 7.45 (d, $J_{ortho} = 7.5$ Hz, 2 H, 2'-H and 6'-H), 7.78 (d, $J_{ortho} = 7.5$ Hz, 2 H, 3'-H and 5'-H) ppm. IR: $\tilde{\nu} = 2229$ cm⁻¹ (C≡N). HRMS: calculated for C₁₉H₂₀N₂ [M⁺] 276.16264, found 276.16255.

10: ¹H NMR: $\delta = 0.95$ (t, 3 H, -CH₃), 1.34 (m, 4 H, 2 CH₂), 1.61 (m, 2 H, CH₂), 2.22 (s, 3 H, CH₃), 2.62 (t, 2 H, CH₂), 7.08–7.15 (m, 4 H, 3-H, 5-H, 6-H), 7.50 (d, $J_{ortho} = 7.5$ Hz, 2 H, 2'-H and 6'-H), 7.78 (d, $J_{ortho} = 7.5$ Hz, 2 H, 3'-H and 5'-H). IR: $\tilde{\nu} = 2228$ cm⁻¹ (C≡N). HRMS: calculated for C₁₈H₁₉N [M⁺] 249.15074; found 249.15005.

The Interaction of Acetonitrile Anion with Benzonitrile: Acetonitrile (0.42 mL, 8.1 mmol) was added to sodium amide prepared by the standard procedure from metallic sodium (0.188 g, 8 mmol) in liquid ammonia (50 mL). The mixture was stirred for 5 min, and then nitrile **2** (0.85 mL, 8.3 mmol) was added and the mixture was stirred at –33 °C for 1 h 15 min. Further treatment was performed as described above. The product mixture thus obtained (1.7 g) consisted of nitrile **2** (2.1 mmol) and β -aminocinnamionitrile (**11**; 5.8 mmol, 94% of consumed monitrile **2**). Nitrile **11** was separated as light-yellow needles from nitrile **2** by washing with cold hexane (3 $\times$ 1.5 mL). Further crystallisation from hexane/benzene (5:1 volume ratio) gave **11** as white needles (0.70 g, 4.9 mmol), m.p. 87 °C (84–87 °C^[30]).

11: ¹H NMR: $\delta = 4.23$ (s, 1 H, =CH), 6.19 (br. s, 2 H, NH₂), 7.43–7.49 (m, 3 H, 3-H, 4-H, 5-H), 7.64 (dd, $J_{ortho} = 7.5$, $J_{meta} = 3.0$ Hz, 2 H, 2-H, 6-H) ppm.

Modelling of the Diffusional Encounter Between RAs **1**²⁻ and **2**²⁻:

a) Liquid ammonia (30 mL) was condensed into two three-necked flasks each supplied with a stirring rod, a bubbler and a gas vent. Dinitrile **1** (0.32 g, 2.5 mmol) and metallic sodium (0.05 g, 2.2 mmol) were put into one of the flasks under argon. The formation of a dark-green solution in 2 min showed the generation of the RA **1**²⁻ salt. Another flask was charged under argon with nitrile **2** (0.26 mL, 2.5 mmol) and sodium (0.05 g, 2.2 mmol). The dark-red solution of RA **2**²⁻ salt formed in 2 min was kept stirring for 1 min and then poured into the flask containing the solution of RA **1**²⁻ salt. The mixture of RAs thus obtained was kept stirring for 3 h at between –40 and –35 °C and processed as described above. The resultant mixture (0.46 g) contained dinitrile **1** (1.5 mmol), *p*-cyanobenzamide (0.2 mmol) and nitrile **2** (2.3 mmol).

b) Liquid ammonia (40 mL) was condensed into a three-necked flask containing a stirring rod, a bubbler and a gas vent. Mononitrile **2** (0.53 mL, 5.1 mmol) and metallic sodium (0.115 g, 5 mmol) were added under argon, and stirring of the reaction mixture for 2 min resulted in formation of a dark-red solution of the RA **2**²⁻ salt. A solution of dinitrile **1** (0.32 g, 2.5 mmol) in THF (17 mL) was immediately added dropwise over 15 min and the mixture was stirred for 2 h at –35 °C. Quenching of the reaction mixture was performed in two ways – by contact with air or by addition of butyl bromide (0.53 mL, 5.1 mmol). Further treatment was performed as described above. The product mixture obtained in the first case (0.52 g) was composed of dinitrile **1** (0.5 mmol), nitrile **2** (3.6 mmol) and 1-cyanocyclohexa-2,5-diene (0.8 mmol), whereas the second product mixture (0.68 g) consisted of butyl bromide (2.0 mmol), nitrile **2** (1.6 mmol), butylbenzene (1.1 mmol), 1-butyl-1-cyanocyclohexa-2,5-diene (0.15 mmol), dinitrile **1** (0.25 mmol), *p*-butylbenzonitrile (0.1 mmol) and 2-butyl-1,4-dicyanobenzene (0.1 mmol).

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