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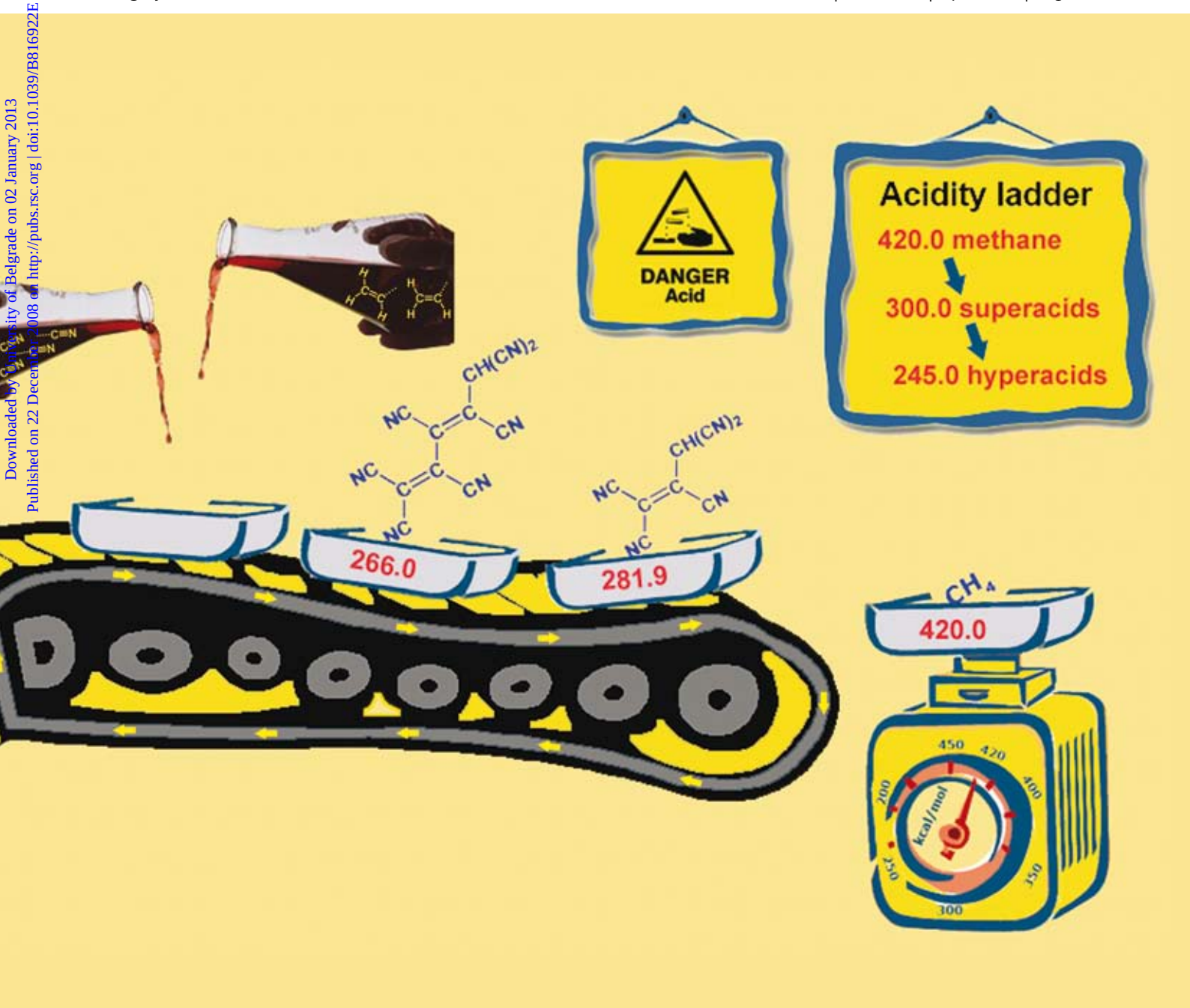

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PAPER

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a DFT-B3LYP study of open chain polycyanopolyenes

The engineering of powerful non-ionic superacids *in silico*—a DFT-B3LYP study of open chain polycyanopolyenes

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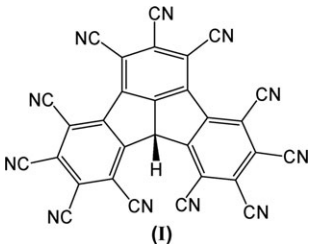
The acidity of a number of all-*trans* polyenes, and some of their phenyl and naphthyl derivatives, was examined by the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) method. A dramatic increase in their acidity was established upon multiple cyanation. The origin of the acidity amplification was identified as the increased stability of the resulting conjugate bases, which is mirrored in Koopmans' term appearing in the triadic analysis. It is important to emphasize that many of the studied polycyano compounds have already been synthesized. Others are probably synthesizable and their preparation is strongly recommended. Some of the examined systems come close to the acidity threshold of 245 kcal mol^{-1} that characterizes hyperacids. The acidity of different tautomeric forms of the same organic acid is briefly discussed.

Introduction

Superacids are invaluable catalysts, both in academic research and in many industrial processes.[1–3] They were first referred to as early as 1927 by Hall and Conant.[4] According to Gillespie and Peel, superacids are substances that are more acidic than 100% sulfuric acid, which is considered to be a reference superacid itself (having a Hammett acidity function of $H_0 \leq -12$).[5,6] The gas phase superacidity threshold of 300 kcal mol^{-1}, the acidity of perchloric acid, $HClO_4$, was recently proposed by the present authors.[7] The application of superacids in organic chemistry were championed by Olah *et al.*,[1–3,8] leading to an outburst of carbocation chemistry. The most popular superacids of the seventies and eighties were mineral acids. More specifically, they were complex systems formed by Lewis acids like SbF_5, TaF_5, *etc.*, and fluorinated Brønsted acids, such as HF, HSO_3F, CF_3SO_3H, *etc.*, which in turn greatly increased the acidity of these hybrid clusters. The best known[9] clusters are HF–SbF_5 and HSO_3F–SbF_5 (magic acid), which exhibit $H_0 \leq -23$. Their structure in solutions of solvents like SO_2 or SO_2ClF depends on their concentration.[10,11] At higher concentrations, adducts of SbF_6^- anions are observed, with a tendency towards complexation with weak bases. Even in highly dilute solutions, the $H^+[SbF_6]^-$ clusters form networks of hydrogen-bonded HF chains.[12] Inorganic (super)acids exhibit, in general, considerable intramolecular charge transfer, implying a pronounced variation of the atomic charges in the isolated gas phase state. This is particularly enhanced in some of the Lewis–Brønsted clusters mentioned above. Additionally, deprotonation in solution amplifies the variation in atomic charges, which is the reason behind the undesirably high susceptibility towards complexation. Hence, inorganic superacids are effective, but under extreme experimental conditions. Consequently, a lot of effort has been devoted to designing alternative substances exhibiting strong acidity, which would be active under mild conditions. Among these, one should emphasize "strong yet gentle" carborane acids, which yield inert anions of very low coordination strength.[13–15] Good candidates are neutral organic superacids, which have either been prepared by using $-CF_3$[16] or some other electron superacceptor substituents,[17,18] or studied by polycyano substitutions of known organic compounds.[19–23] The cyano group has proved to be very useful in view of its strong σ- and π-electron withdrawing power, and its modest steric requirements. A judicial choice of molecular framework, combined with polycyanation, has lead to the hyperacid, **I** (Scheme 1), which is 43 and 40 orders of magnitude stronger as an acid in the gas phase than H_2SO_4 and $HClO_4$, respectively.[7] Its gas phase deprotonation enthalpy assumes the value ΔH_{acid} = 246.3 kcal mol^{-1}. This undecacyano derivative of fluoradene, $HC_{19}(CN)_{11}$, is the strongest neutral organic superacid designed *in silico* so far.[7]

The adopted terminology deserves a word of comment. Firstly, neutral organic (super)acids denote the uncharged species. Secondly, the term implies a small to moderate intramolecular charge transfer in the original (initial) acid. Interestingly enough, it turns out that the excess negative



(I)

Scheme 1 Undecacyanofluoradene (**I**), the first neutral organic hyperacid.

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charge is also very effectively dispersed in the corresponding conjugate base, meaning that the charge variation remains persistently small or moderate, even in the anion. This has a number of favorable consequences, including a low nucleophilicity of the conjugate bases. Concomitantly, the gas phase geometries are transferable to solutions, provided that solvents of medium polarity are used. Since strong organic acids possess some distinct advantages over their mineral counterparts that are central to general acid catalysis in mild chemical environments,[24] we deemed it worthwhile to continue our studies of polycyano-substituted hydrocarbons in a systematic way, focusing here on polyenes. The impetus is given by the fact that a number of these compounds have been synthesized (*vide infra*), albeit many times in deprotonated anionic forms.

Computational details

Acidity is calculated in a standard way as the enthalpy change, ΔH_{acid}, for the gas phase (g) reaction:

$$AH(g) \rightarrow A^-(g) + H^+(g) \quad (1)$$

It has two contributions:

$$\Delta H_{acid} = \Delta E_{acid} + \Delta(pV) \quad (2)$$

where ΔE_{acid} is the change in the total molecular energy of acid AH, its conjugate base A^- and the proton according to eqn (1), and it includes the zero-point vibrational energy (ZPVE) and the finite temperature (298.15 K) corrections. The second term, $\Delta(pV)$, stands for the pressure–volume work contribution, which is equal to RT. The translational energy of the proton is $\frac{3}{2}RT$, yielding the total, $H_{tot}(H^+) = \frac{5}{2}RT$. The ZPVE and temperature corrections were computed at the B3LYP/6-31G(d) level along with the optimization of the spatial structures. The final total electronic energies were obtained by single-point B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) calculations. It is worth bearing in mind that stronger acids possess smaller values of ΔH_{acid}(AH) and the corresponding proton affinity, PA(A^-), which implies an easier release of the acidic proton.

In order to get an insight into the origin of acidity in polycyanated polyenes, we performed a trichotomy analysis.[25] The proton affinity of the anion A^-, representing the conjugate base, is given by:

$$PA(A^-) = -IE(A^-)_1{}^{ad} + EA(H^+)_1{}^{ad} + (BDE)^\bullet{}_{AH} \quad (3)$$

where $IE(A^-)_1{}^{ad}$ and $EA(H^+)_1{}^{ad}$ denote the first adiabatic ionization energy of the anion obtained by deprotonation and the first adiabatic electron affinity of the proton, respectively, and $(BDE)^\bullet{}_{AH}$ is the homolytic bond dissociation energy upon hydrogen atom release from the acid. It is useful for interpretative purposes to break down the $IE(A^-)_1{}^{ad}$ term into two contributions:

$$-IE(A^-)_1{}^{ad} = -IE(A^-)_n{}^{Koop} + E(ei)^{(n)}{}_{rex} \quad (4)$$

where $IE(A^-)_n{}^{Koop}$ is the ionization energy of electron ejection from the nth molecular orbital (MO) that accommodates the excess electron in the sudden Koopmans' approximation,[26] and $E(ei)^{(n)}{}_{rex}$ is the geometrical and electronic relaxation energy upon ionization of the anion in real time. Koopmans' theorem[26] states that the ionization energy (equal to the negative MO energy of the MO hosting the electron to be expelled) is approximate, but it works reasonably well, as evidenced by the abundant experimental data gathered by photoelectron spectroscopy. Hence, the $IE(A^-)_n{}^{Koop}$ term gives an instant snapshot of the frozen electrons and nuclei in the final state of the deprotonation process. In other words, Koopmans' term mirrors the properties of the conjugate base anion. It appears that the increased stability of the latter significantly contributes to the overall acidity of the acid, AH. The Koopmans' ionization energies were calculated by the HF/6-311+G(2d,p)//B3LYP/6-31G(d) model, whereas the resulting molecular radicals, $A^\bullet$, were treated by the unrestricted UB3LYP/6-311+G(2d,p)//UB3LYP/6-31G(d) method. Taking into account eqn (3) and eqn (4), and the fact that $EA(H^+)_1{}^{ad} = 313.6$ kcal mol^{-1}, one obtains:

$$PA(A^-) = -IE(A^-)_n{}^{Koop} + E(ei)^{(n)}{}_{rex} + (BDE)^\bullet{}_{AH} + 313.6 \text{ kcal mol}^{-1} \quad (5)$$

which will be used to interpret the acidities. Finally, we are usually interested in trends of changes obtained by relative values against the reference molecule, in this case:

$$\begin{aligned} PA(A_M^-) - PA(A_{ref}^-) &= \Delta[PA(A_M^-)] \\ &= [-\Delta IE(A_M^-)_n{}^{Koop}; \\ &\quad \Delta E(ei)(A_M^-)^{(n)}{}_{rex}; \\ &\quad \Delta(BDE)(A_M^-)^\bullet{}_{AH}] \end{aligned} \quad (6)$$

where subscripts M and ref denote the molecule under study, and the gauge reference molecule, respectively. The square parentheses imply summation of the three terms, and the different terms are separated by semicolons.

All computations were carried out using the GAUSSIAN 03 program package.[27]

Results and discussion

The studied cyanopolyenes are depicted in Fig. 1. They are supplemented by the methyl anion (**1**) cyanomethanes **2–4**, and cyanoethanes **5** and **6**, which are included for the sake of completeness. Since we consider deprotonation to be the reverse of protonation, the conjugate bases A^- are presented. They are protonated at various positions, denoted by small letters a, b, c, *etc*. If the proton is attached at the formally denoted anionic atom (always labeled as a), then a new C–H chemical bond is formed and the CH acid is the outcome. However, we found that in the extended π-electron planar anions, *e.g.* in the paradigmatic pentacyanocyclopentadiene anion, $[C_5(CN)_5]^-$, the most basic atom is the nitrogen of the cyano group.[28] In that case, the keteneimine moiety, ═C═N–H, is obtained upon protonation and the resulting acid is the NH one. This seems to be a frequent occurrence, as shown by a number of studies,[29–31] and it was found in the present work too (*vide infra*).

It is extremely important to emphasize that a large number of the examined systems have been previously synthesized (those drawn inside the rectangular boxes in Fig. 1), but predominantly in deprotonated anionic forms stabilized by the presence of positively charged counterions. The relevant experimental work is documented in refs. 32–41. The

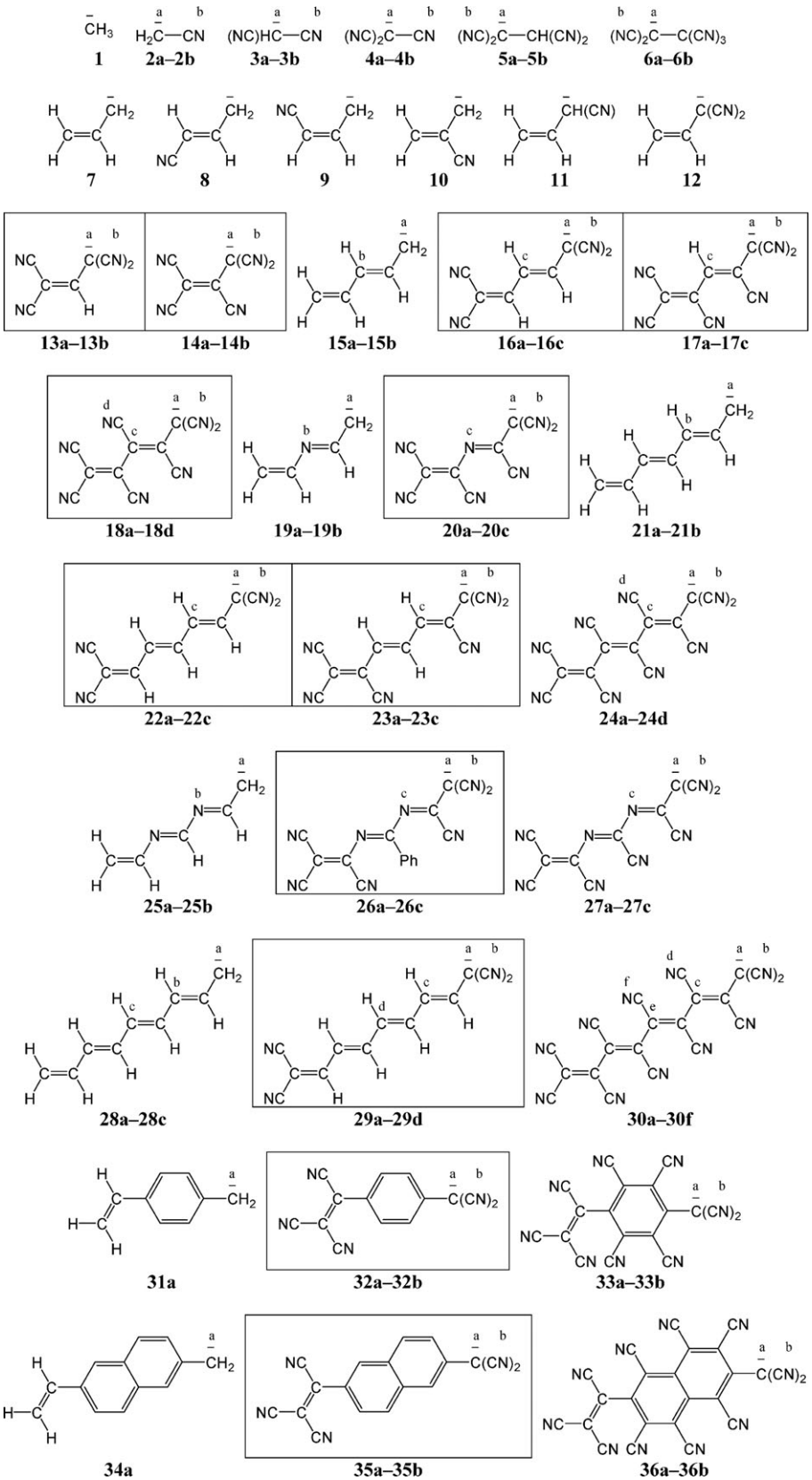


Fig. 1 A schematic representation of the molecules studied in this work. Small letters a, b, c, *etc*. denote the site of the proton attack. Polycyano compounds that have already been synthesized are drawn inside the rectangular boxes.

impressive number of synthesized cyanopolyenes[32–41] gives rise to optimism that even larger π-systems could be poly-cyanated too. Some recent advances in the preparation of cyano-substituted compounds,[42–46] in addition to the

classical articles of Ciganek *et al.*[47] and others,[48–51] have been reported.

The total energies and ΔH_{acid} values of the anions and their protonated neutral forms are given in Table 1. Let us briefly comment on the substituted methanes. They have been studied previously by the G2(MP2) method[28] and their acidities have been recalculated in the present computational study in order to obtain consistent and comparable results for the set of molecules under scrutiny. Perusal of the presented data shows that the agreement with available experimental acidities[52] is very good (Table 1). An insight into their acidity was obtained by triadic analysis, selecting $\mathbf{1}^-$ as a reference conjugate base (Table 2). The amplification of acidity upon cyanation is described by the differences: $\Delta[PA(\mathbf{2a}^-) - PA(\mathbf{1}^-)] = [-19.9; -15.7; -10.4] = -46.0$, $\Delta[PA(\mathbf{3a}^-) - PA(\mathbf{1}^-)] = [-50.0; -14.9; -20.3] = -85.3$ and $\Delta[PA(\mathbf{4a}^-) - PA(\mathbf{1}^-)] = [-78.9; -9.9; -30.2] = -119.0$ kcal mol^{-1}. The influence of the cyano group is very strong and is dramatic in $C(CN)_3^-$. This makes $HC(CN)_3$ the simplest superacid, because its $PA[C(CN)_3^-] = 294.6$ kcal mol^{-1}, which is lower than 300 kcal mol^{-1}. This is a result of the concerted action of all three terms, with an overwhelming Koopmans' contribution of -78.9 kcal mol^{-1}. In other words, within Koopmans' model, it becomes harder to eject an electron from the anion with every additional cyano group that is attached to the carbanionic centre, since the anions become more stable with an increasing number of cyano substituents, leading to an increase in acidity. This contribution quantitatively prevails over the remaining two terms that appear in the triadic analysis, therefore meaning that the properties of the final state are decisive for such trends in the acidity of cyanomethanes. It is also worth pointing out that by attaching just three cyano groups to the parent methane molecule, we transform one of the least acidic compounds in the gas-phase (CH_4) into a superacid ($HC(CN)_3$), reducing the deprotonation enthalpy by almost 120 kcal mol^{-1}. Obviously, the anions of hydrocarbons that are polysubstituted by cyano groups possess a very low proton affinity and a high acidity. A similar situation occurs in substituted ethanes **5a** and **6a**, where the $PA(A^-)$ values are 304.1 and 295.8 kcal mol^{-1}, respectively. It follows that $HC(CN)_2$–$CH(CN)_2$ and $HC(CN)_2$–$C(CN)_3$ are above and below the superacidity threshold of 300 kcal mol^{-1} by 4 kcal mol^{-1}, respectively. The latter compound is a superacid due to the cooperative action of five cyano groups. Taking into account the $PA(CH_3CH_2^-)$ value of the parent ethane (419.5 kcal mol^{-1}), and the corresponding IE_n^{Koop}, $E(ei)^{(n)}_{rex}$ and $(BDE)^\bullet$ values of 19.5, 25.7 and 99.6 kcal mol^{-1}, respectively, one easily deduces the differences: $PA(\mathbf{5a}^-) - PA(CH_3CH_2^-) = [-90.0; -7.8; -17.5] = -115.3$ and $PA(\mathbf{6a}^-) - PA(CH_3CH_2^-) = [-102.1; -5.0; -16.5] = -123.6$ kcal mol^{-1}. This is in accordance with a general picture that in strong (super)acids, all three terms contribute to an enhanced acidity, the influence of the first term being overwhelming. It should be noted in passing that the experimental $PA(CH_3CH_2^-)_{EXP} = 420.0 \pm 2.0$ kcal mol^{-1},[52] which is in good accordance with the calculated value of 419.5 kcal mol^{-1}.

It is interesting to take into account the difference in acidity between **2a** and CH_3–$C(CN)_3$. The latter assumes the value $\Delta H_{acid}[\mathbf{2a}] - \Delta H_{acid}[CH_3\text{–}C(CN)_3] = 371.7 - 364.0 = 7.1$ kcal mol^{-1}. It appears that the tricyanomethyl group exhibits an even larger acidifying effect on a neighboring deprotonation center than the cyano group, the difference being around 7 kcal mol^{-1}. This is not surprising, since the tricyanomethyl group is a stronger electron-withdrawing substituent than the cyano group. The latter is nicely illustrated by the corresponding substituent's σ constants. For example, the σ_m and σ_p constants for the cyano group are 0.56 and 0.66, respectively, whereas the same parameters for the tricyanomethyl group are much higher, assuming the values 0.97 and 0.96, respectively.[53] However, in larger systems and particularly in poly-substituted compounds, the smaller and sterically less demanding cyano groups exert a combined acidifying effect[28] superior to that of tricyanomethyl groups, since the former are much more efficient at stabilizing excess negative charge. To demonstrate this, one needs to consider the gas phase acidity of $HC[C(CN)_3]_3$. Our B3LYP calculations show that the corresponding ΔH_{acid} is 297.9 kcal mol^{-1}, which makes this compound less acidic than **4a**, whose $\Delta H_{acid}[HC(CN)_3]$ is 294.7 kcal mol^{-1} (Table 1).

The strong acidifying effect of the cyano group can be further illustrated by the triadic analysis of **7** as the simplest π-system, and its 1-cyano derivative, **8**. First of all, it turns out that **7** is significantly more acidic than **1**. Triadic analysis, $PA(\mathbf{7}^-) - PA(\mathbf{1}^-) = [14.7; -25.6; -19.0] = -29.9$ kcal mol^{-1}, revealed that the Koopmans' term, which mirrors properties of the final state, predicts methane to be more acidic than propene. However, the other two terms prevail and are responsible for increased acidity. The difference, $PA(\mathbf{8}^-) - PA(\mathbf{7}^-) = [-32.6; 2.5; -2.6] = -32.7$ kcal mol^{-1}, suggests that the cyanation of propene, as in **8**, leads to enhancement of the acidity by 32.7 kcal mol^{-1}, because of the higher Koopmans' ionization energy (by 32.6 kcal mol^{-1}), meaning that the HOMO energy is lower by this amount (Fig. 2). Consequently, the resulting anion is more stable. This is a result of anionic resonance between the anionic $–CH_2^-$ center and the –CN fragment (Fig. 3(a)). The remaining two terms in the triadic analysis, $\Delta E(ei)^{(n)}_{rex}$ and $\Delta(BDE)^\bullet_{AH}$, cancel out. Moreover, it turns out that the PAs of $\mathbf{8}^-$ and $\mathbf{9}^-$ are very similar, implying that the anionic resonance is equally effective, irrespective of the *trans*- or *cis*-position of the cyano group attached to the C1 carbon atom of propene. This is intuitively expected, because the formal negative charge and the cyano group are separated by alternating single and double bonds in both cases, which is a prerequisite for an efficient charge (either negative or positive) resonance effect. A different situation occurs in **10**, where the negative charge and the π-system of the cyano group are separated by two formally single bonds. Therefore, it is not surprising that the Koopmans' ionization energy is lower in **10** by 12.1 and 10.9 kcal mol^{-1} relative to **8** and **9**, respectively. Still, it is 20.5 kcal mol^{-1} larger than that in **7**, thus indicating a significant contribution from the diradical valence bond structure given in Fig. 3(b). Consequently, **10** is less acidic than **8** and **9**, but it is significantly more acidic than the parent molecule, **7** (Table 2). The most acidic mono-cyano derivative of propene **7** is compound **11**, which has a cyano group attached directly to the deprotonated centre. This is due to a smaller

Table 1 The total molecular energies of the studied molecules in the gas phase (GP), E_{GP}, obtained at the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) level of theory. H_{corr} denotes the thermal correction to the enthalpy obtained by the B3LYP/6-31G(d) model. The experimental deprotonation enthalpies, $\Delta H_{acid,EXP}$, are taken from ref. 52

Molecule	E_{GP}/a.u.	H_{corr}/a.u.	ΔH_{acid}/kcal mol^{-1}	$\Delta H_{acid,EXP}$/kcal mol^{-1}
1	−40.53486	0.04901	417.8	418.0 ± 3.5
1$^-$	−39.85414	0.03167	—	—
2a	−132.79881	0.05018	371.7	372.9 ± 2.1
2b	−132.76130	0.04845	349.3	—
2$^-$	−132.19386	0.03528	—	—
3a	−225.04741	0.05066	329.9	335.8 ± 2.1
3b	−225.02722	0.04953	317.9	—
3$^-$	−224.51060	0.03721	—	—
4a	−317.28417	0.05060	294.7	—
4b	−317.28188	0.05005	293.7	—
4$^-$	−316.80463	0.03841	—	—
5a	−448.86805	0.08072	304.3	—
5b	−448.85583	0.07996	297.1	—
5$^-$	−448.37254	0.06779	—	—
6a	−541.09811	0.08003	295.9	—
6b	−541.08806	0.07928	290.1	—
6$^-$	−540.61593	0.06709	—	—
7	−117.94858	0.08510	387.9	389.1 ± 1.5
7$^-$	−117.31625	0.06858	—	—
8	−210.22003	0.08588	355.2	—
8$^-$	−209.64181	0.07129	—	—
9	−210.22011	0.08597	356.6	—
9$^-$	−209.63953	0.07125	—	—
10	−210.21775	0.08575	369.6	370.7 ± 2.1
10$^-$	−209.61490	0.06951	—	—
11	−210.21134	0.08582	349.7	—
11$^-$	−209.64181	0.07129	—	—
12	−302.45963	0.08594	316.6	—
12$^-$	−301.94428	0.07284	—	—
13a	−486.97338	0.08683	281.6	—
13b	−486.97309	0.08600	281.9	—
13$^-$	−486.51482	0.07461	—	—
14a	−579.22209	0.08676	274.4	—
14b	−579.22180	0.08583	274.8	—
14$^-$	−578.77480	0.07440	—	—
15a	−195.37582	0.12086	371.0	369.2 ± 1.2
15b	−195.36300	0.12085	363.0	—
15$^-$	−194.77094	0.10493	—	—
16a	−564.41038	0.12285	281.1	—
16b	−564.40641	0.12203	279.1	—
16c	−564.41333	0.12296	282.9	—
16$^-$	−563.95238	0.11041	—	—
17a	−748.90984	0.12286	269.3	—
17b	−748.90599	0.12187	267.5	—
17c	−748.91885	0.12301	274.9	—
17$^-$	−748.47063	0.11044	—	—
18a	−841.14838	0.12257	260.9	—
18b	−841.15166	0.12171	263.5	—
18c	−841.15268	0.12279	263.4	—
18d	−841.15564	0.12164	266.0	—
18$^-$	−840.72261	0.11016	—	—

Table 1 (*continued*)

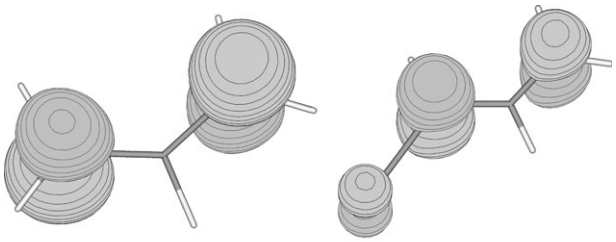
Molecule	E_{GP}/a.u.	H_{corr}/a.u.	ΔH_{acid}/kcal mol^{-1}	$\Delta H_{acid,EXP}$/kcal mol^{-1}
19a	−211.41833	0.10871	361.8	—
19b	−211.41651	0.10920	360.3	—
19$^-$	−210.82925	0.09384	—	—
20a	−764.94166	0.11041	263.4	—
20b	−764.94488	0.10962	265.9	—
20c	−764.96600	0.11137	278.0	—
20$^-$	−764.51199	0.09808	—	—
21a	−272.80482	0.15663	360.3	364.8 ± 3.1
21b	−272.78926	0.15647	350.7	—
21$^-$	−272.21739	0.14105	—	—
22a	−641.84402	0.15876	282.1	—
22b	−641.83740	0.15790	278.5	—
22c	−641.84579	0.15881	283.1	—
22$^-$	−641.38427	0.14615	—	—
23a	−826.35497	0.15899	271.4	—
23b	−826.34712	0.15808	267.1	—
23c	−826.35453	0.15901	271.2	—
23$^-$	−825.91217	0.14641	—	—
24a	−1103.07858	0.15845	258.0	—
24b	−1103.08259	0.15745	261.1	—
24c	−1103.08249	0.15866	260.3	—
24d	−1103.08516	0.15744	262.8	—
24$^-$	−1102.65718	0.14585	—	—
25a	−304.89193	0.13263	345.3	—
25b	−304.89254	0.13355	345.1	—
25$^-$	−304.32999	0.11859	—	—
26a	−1089.54465	0.22018	266.2	—
26b	−1089.54243	0.21932	266.8	—
26c	−1089.56574	0.22074	280.6	—
26$^-$	−1089.10776	0.20752	—	—
27a	−950.66497	0.13422	253.8	—
27b	−950.66935	0.13336	257.1	—
27c	−950.68605	0.13511	266.5	—
27$^-$	−950.25045	0.12183	—	—
28a	−350.23447	0.19241	352.6	—
28b	−350.21825	0.19224	342.6	—
28c	−350.21643	0.19228	341.4	—
28$^-$	−349.65950	0.17704	—	—
29a	−719.27643	0.19461	282.8	—
29b	−719.26831	0.19373	278.2	—
29c	−719.27830	0.19473	283.9	—
29d	−719.27837	0.19473	283.9	—
29$^-$	−718.81541	0.18187	—	—
30a	−1365.01159	0.19438	255.6	—
30b	−1365.01144	0.19339	256.1	—
30c	−1365.01511	0.19450	256.2	—
30d	−1365.01551	0.19331	258.7	—
30e	−1365.01481	0.19449	257.5	—
30f	−1365.01495	0.19328	258.4	—
30$^-$	−1364.59384	0.18158	—	—
31a	−349.06790	0.17085	370.3	—
31$^-$	−348.46426	0.15495	—	—
32a	−810.35450	0.17269	283.9	—
32b	−810.34768	0.17202	280.1	—
32$^-$	−809.89194	0.16022	—	—
33a	−1179.35869	0.17233	274.0	—
33b	−1179.35582	0.17143	272.7	—
33$^-$	−1178.91159	0.15949	—	—

Table 1 (*continued*)

Molecule	E_{GP}/a.u.	H_{corr}/a.u.	ΔH_{acid}/kcal mol^{-1}	$\Delta H_{acid,EXP}$/kcal mol^{-1}
34a	−502.74995	0.22030	365.9	—
34$^-$	−502.15349	0.20453	—	—
35a	−964.04006	0.22219	288.8	—
35b	−964.03014	0.22147	283.0	—
35$^-$	−963.56952	0.20956	—	—
36a	−1517.53574	0.22165	270.0	—
36b	−1517.53356	0.22074	269.2	—
36$^-$	−1517.09484	0.20872	—	—

Table 2 The contributions to the proton affinities, PA(A^-), obtained by triadic analysis (kcal mol^{-1})

Molecule	IE(A^-)$_n^{Koop}$	IE(A^-)$_1^{ad}$	$E(ei)^{(n)}_{rex}$	$(BDE)_{AH^\bullet}$	PA(A^-)
1$^-$	$(27.9)_1$	0.2	27.7	104.2	417.6
2a$^-$	$(47.8)_1$	35.8	12.0	93.8	371.6
3a$^-$	$(77.9)_1$	67.8	10.1	83.9	329.7
4a$^-$	$(106.8)_1$	93.0	13.8	74.0	294.6
5a$^-$	$(109.5)_1$	91.6	17.9	82.1	304.1
6a$^-$	$(121.6)_1$	100.9	20.7	83.1	295.8
7$^-$	$(13.2)_1$	11.1	2.1	85.2	387.7
8$^-$	$(45.8)_1$	41.2	4.6	82.6	355.0
9$^-$	$(44.6)_1$	40.3	4.3	83.1	356.4
10$^-$	$(33.7)_1$	31.7	2.0	87.5	369.4
11$^-$	$(44.6)_1$	40.3	4.3	77.4	350.7
12$^-$	$(74.3)_1$	66.1	8.2	69.0	316.5
14$^-$	$(124.1)_1$	110.7	13.4	71.3	274.2
15$^-$	$(21.8)_1$	21.9	0.1	79.2	370.9
18$^-$	$(136.6)_1$	122.5	14.1	69.6	260.7



7$^-$ **8**$^-$

Fig. 2 A comparison of selected HOMOs and their orbital energies in propene anion **7**$^-$ and 1-cyanopropene anion **8**$^-$.

bond dissociation energy of 5.2 kcal mol^{-1} relative to **8** [PA(**11**$^-$) − PA(**8**$^-$) = [1.2; −0.3; −5.2] = −4.3 kcal mol^{-1}].

In considering the acidities (PAs of their anions) of compounds **12–18**, let us use the compact notation given by eqn (6) in units of kcal mol^{-1}. An enormous increase in acidity is obtained by double cyano substitution at the CH_3 group of propene, as in **12**, relative to **7**. The breakdown into its components is given by Δ[PA(**12**$^-$)] = [−61.1; 6.1; −16.2]

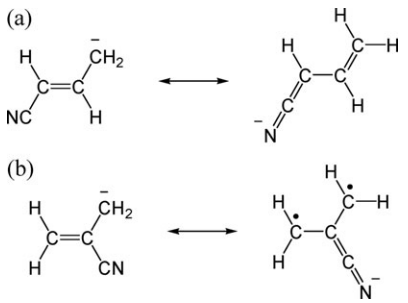


Fig. 3 The resonance structures of (a) 1-cyanopropene anion **8**$^-$ and (b) 2-cyanopropene anion **10**$^-$.

= −71.2, yielding PA(**12**$^-$) = 316.5 kcal mol^{-1}. This indicates that additional cyanation would produce superacids. This is indeed already the case in **14**, where the PA assumes a value as low as 274.2 kcal mol^{-1}. Triadic analysis yields Δ[PA(**14**$^-$)] = [−110.9; 11.3; −13.9] = −113.5 kcal mol^{-1}, meaning that the lion's share of the increased acidity, relative to parent propene **7**, is derived from single orbital stabilization of the MO containing the excess electron in anion A^-, which is as high as −110.9 kcal mol^{-1}. A much smaller, but still significant, contribution towards acidity enhancement (−13.9 kcal mol^{-1}) is provided by the decreased bond dissociation energy. It is interesting to observe that the difference in acidity between compounds **14** and **13** is 7.2 kcal mol^{-1}, whereas the variation of acidity in an analogous pair of compounds, **10** and **7**, is 18.3 kcal mol^{-1}. The fact that an acidifying effect of the β-cyano group in the former case is reduced by more than half compared to that in **10** can be attributed to the steric crowding of the remaining four cyano groups in compounds **14** and **13**, which in turn, prevents more efficient anionic resonance. Extension of the π-system, leading to **15**, gives a modest increase in the acidity, as shown by ΔPA(**15**$^-$) = PA(**15**$^-$) − PA(**7**$^-$) = [−8.6; −2.0; −6.0] = −16.6 kcal mol^{-1}. However, heptacyanation of **15** yields a strong superacid with a ΔH_{acid}(**18**) value of 260.7 kcal mol^{-1}. The triadic component analysis gives ΔPA(**18**$^-$) = PA(**18**$^-$) − PA(**7**$^-$) = [−123.4; 12.0; −15.6] = −127.0 kcal mol^{-1}, revealing that the final state effect realized by stabilization of the negatively charged conjugate base exerts by far the largest influence, which holds as a rule in other extended π-systems. Therefore, we shall discuss in what follows only their ΔH_{acid} values. It is interesting to reveal the trend of the increase in

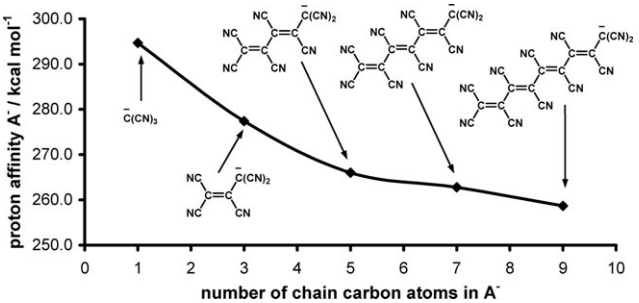


Fig. 4 The acidity of polycyano-substituted polyenes in relation to the size of their chain.

acidity as a function of the number of carbon atoms in the polyene backbone (Fig. 4). The PA values of conjugate bases A^-, where A^- represents **4a**$^-$, **14a**$^-$, **24a**$^-$ and **30a**$^-$, are 294.7, 274.4, 262.8 and 258.7 kcal mol^{-1}, respectively, providing convincing evidence that multiply cyanated zig-zag polyenes are powerful organic superacids. The number of cyano groups is decisive; however, their variation due to deprotonation at different positions within the same molecular framework leads to acids of various strengths, which is also useful in forming a dense ladder of superacids.

It is remarkable that the $-CH(CN)_2$ group attached to phenyl and naphthyl moieties in **33** and **36** also yields strong superacids. Slightly less acidic, but still well below the superacidity threshold, are compounds **32** and **35**, whose acidity constants take values of 283.9 and 288.8 kcal mol^{-1}, respectively. It has to be iterated that both of these compounds have already been synthesized as conjugate bases.[40,41] The cyano effect in **33a** enhances its acidity by 96.3 kcal mol^{-1} relative to parent hydrocarbon system **31a**. Similarly, **36a** is more acidic than **34a** by 95.9 kcal mol^{-1}. This is in accordance with our earlier finding that the anionic resonance effect stabilizes the molecular framework, irrespective of whether it is aromatic or antiaromatic, provided it is functionalized with cyano groups.[7,21,22,29]

Finally, let us briefly comment on the different positions of protonation of the polycyanopolyene anions. If a polyene anion is attacked at various sites α = a, b, c, *etc*., different acids are obtained. These acids have different acidities, but one thing is in common: their final state (deprotonated anion) is the same. This means that their acidity is determined by the $(BDE)^{\bullet}_{\alpha}$ term. The acidities can significantly differ between tautomers, like in the case of **3a** and **3b**. This is obvious because protonation at position **a** leads to $(CN)CH_2-CN$, whereas protonation at position **b** produces the keteneimine fragment, =C=NH, and a concomitant planar system, (CN)HC=C=NH, which is less stable by 12 kcal mol^{-1} in total molecular enthalpy at 298.15 K. In other cases, the $(BDE)^{\bullet}$ values are very similar and consequently the resulting acidities are almost the same (*viz*. **4a**$^-$ and **4b**$^-$, or **13a**$^-$ and **13b**$^-$). Anion **17**$^-$ is very interesting, because the proton will attack the central carbon atom of the 1,3-butadiene framework, leading to a methane substituted by two equivalent $-C(CN)=C(CN)_2$ fragments. The resulting superacid has a ΔH_{acid}(**17c**) of 275 kcal mol^{-1}. Another system of interest is **18**$^-$, where all four positions, **a–d**, are highly acidic, making

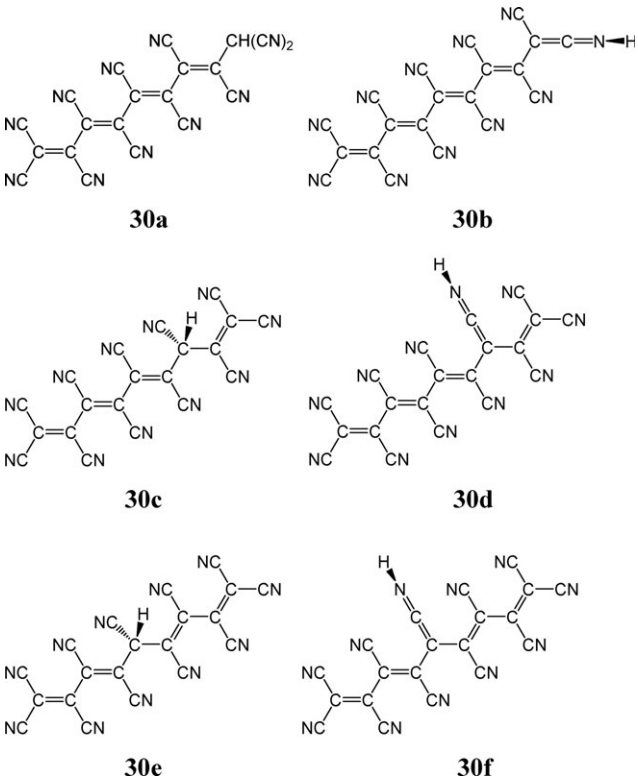


Fig. 5 The tautomeric forms of compound **30**, which represents the most powerful superacidic system investigated in this work.

this system a very powerful superacid. The structures resulting from proton attack at all four positions can be easily deduced and need not be depicted in a separate figure. The same holds for other compounds and the numbers presented in Table 1 speak for themselves. One last example, however, deserves particular attention, this being the largest polyene studied, **30**$^-$. Protonation at positions **a–f** lead to structures **30a–30f**, which are pictorially shown in Fig. 5. It is remarkable indeed that these various structures have very similar acidities, which are spaced in a narrow range of 255.6–258.4 kcal mol^{-1}. These are the most acidic compounds studied in this work, and the range of their acidities implies that they approach the hyperacidity threshold[7] of 245 kcal mol^{-1}, being short by some 10 kcal mol^{-1}.

Concluding remarks

A systematic study of the acidity of zig-zag polyenes, and some of their phenyl and naphthyl derivatives by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method has been performed. It was shown that their partial or complete cyano substitution yields strong or very powerful superacids. An important point is that many of the studied compounds have been previously synthesized (depicted inside the rectangular boxes in Fig. 1). Practically all of the synthesized compounds exhibit pronounced superacidity, the most acidic being compound **18**, with ΔH_{acid}(**18d**) = 266.0 kcal mol^{-1}. Other molecules investigated here are strongly recommended for preparation, since they would give new superacids. If some of the acids are too strong to be obtained in a neutral form,

then their stable anions would probably be feasible. Since anions of organic π-systems have a very effectively dispersed electron density of the extra electron (*viz*. refs. 7, 19–22 and 28–31), they should have low nucleophilicities. This means that their aggressiveness in solution should be diminished and they might be useful as ligands of very low coordination power, which would be convenient in the design of some new materials.

The nature of the increased acidity of multiply cyanated polyenes was examined by a triadic formula. It was found that an overwhelming effect is exerted by the Koopmans' term, implying that efficient and profitable accommodation of the excess charge in molecular orbitals of low orbital energy strongly enhances their acidity. The most powerful superacidic systems are molecules **30a–30f**, which could be obtained from a 1,3,5,7-nonatetraene skeleton dressed with eleven cyano groups. Their gas phase acidities are placed within the narrow range of 255.6–258.4 kcal mol^{-1}, which makes them around 36 and 31 orders of magnitude stronger acids in the gas phase than H_2SO_4 and $HClO_4$, respectively.

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