Supplementary Information

Abbreviations:

MNA	2-methyl-4-nitroaniline
POM	3-methyl-4-nitropyridine *N*-oxide
NPP	*N*-4-nitrophenyl-L-prolinol
PNP	2-(*N*-(L)-prolinol)-5-nitropyridine
pNA	*p*-nitroaniline

Table S1 Details of X-ray diffraction data and multipole refinements.[a]

	benzene[b]	**urea**[c]	**MNA**[d]	**POM**	**NPP**	**PNP**	**pNA**
space group	*Pbca*	$P\bar{4}2_1m$	*Ia*	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1/c$
a / Å	7.409	5.578	8.167	5.123	5.172	5.095	8.471
b / Å	9.454	5.578	11.564	6.100	14.845	14.879	6.020
c / Å	6.781	4.686	7.413	20.876	7.150	6.998	12.087
α / °	90	90	90	90	90	90	90
β / °	90	90	93.31	90	106.06	107.75	92.89
γ / °	90	90	90	90	90	90	90
T / K	110	123	100	100	100	100	100
$\sin(\theta/\lambda)_{max}$ / Å^{-1}	1.11	1.44	1.27	1.12	1.11	1.08	1.14
N_{obs}	1766	817	5055	4007	5769	5214	5344
%$R(F)$	1.89	1.17	1.74	2.22	1.62	1.22	2.47
%$R_w(F)$	1.69	0.64	1.59	1.83	1.23	1.11	2.04
gof	1.04	1.57	1.47	1.97	1.35	1.47	1.87
	4σ	4 σ	4 σ	6 σ	6 σ	6 σ	6 σ

[a] For computation of crystal refractive indices the following room temperature unit cell dimensions were used: benzene (–3°C): E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. R. Soc. Lond. A*, 1958, **247**, 1-21; urea: N. Sklar, M. A. Senko and B. Post, *Acta Crystallogr.*, 1961, **14**, 716; POM: M. Shiro, M. Yamakawa and T. Kubota, *Acta Crystallogr., Sect. B*, 1977, **33**, 1549-1556; NPP: J. Zyss, J. F. Nicoud and M. Coquillay, *J. Chem. Phys.*, 1984, **81**, 4160-4167; PNP: R. J. Twieg and C. W. Dirk, *J. Chem. Phys.*, 1986, **85**, 3537-3543; pNA: H. Y. Qian, Z. G. Yin, J. Jia, N. Zhou and L. Q. Feng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, o5048-o5049; MNA: H. Graafsma, A. Paturle, L. Wu, H. S. Sheu, J. Majewski, G. Poorthuis and P. Coppens, *Acta Crystallogr., Sect. A*, 1992, **48**, 113-120.

[b] X-ray data from H. B. Bürgi, S. C. Capelli, A. E. Goeta, J. A. K. Howard, M. A. Spackman and D. S. Yufit, *Chem.-Eur. J.*, 2002, **8**, 3512-3521.

[c] X-ray data from H. Birkedal, D. Madsen, R. H. Mathiesen, K. Knudsen, H. P. Weber, P. Pattison and D. Schwarzenbach, *Acta Crystallogr., Sect. A*, 2004, **60**, 371-381.

[d] X-ray data from A. E. Whitten, P. Turner, W. T. Klooster, R. O. Piltz and M. A. Spackman, *J. Phys. Chem. A*, 2006, **110**, 8763-8776.

Table S2 Molecular polarizability tensors (au). $\bar{\alpha} = \frac{1}{3} tr(\boldsymbol{\alpha}) = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)$ is the mean polarizability, where α_1, α_2 and α_3 are principal components of the tensor, and κ is the polarizability anisotropy, defined by $\kappa = \frac{1}{\sqrt{2}}\left[(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2\right]^{\frac{1}{2}}$.

molecule		Hartree-Fock	MP2	MP2 + field	XCHF
benzene	α_{xx}	61.47	62.14		63.68
	α_{yy}	76.32	77.81		78.16
	α_{zz}	61.15	61.82		63.35
	α_{xy}	-6.41	-6.75		-6.90
	α_{xz}	-17.54	-18.46		-18.01
	α_{yz}	-6.39	-6.74		-6.53
	$\bar{\alpha}$	66.31	67.25		68.40
	κ	0.188	0.195		0.186
urea	α_{xx}	29.03	32.85	33.17	33.45
	α_{yy}	29.03	32.85	33.17	33.45
	α_{zz}	36.08	41.15	39.98	40.10
	α_{xy}	5.80	7.11	7.75	7.38
	α_{xz}	0.000	0.000	0.000	0.000
	α_{yz}	0.000	0.000	0.000	0.000
	$\bar{\alpha}$	31.38	35.61	35.44	35.67
	κ	0.130	0.139	0.142	0.135
POM	α_{xx}	89.31	92.54	92.43	89.21
	α_{yy}	119.32	136.85	135.09	127.51
	α_{zz}	93.31	99.14	98.73	95.92
	α_{xy}	24.93	29.51	29.06	27.24
	α_{xz}	-17.76	-15.82	-16.12	-17.00
	α_{yz}	24.59	31.95	31.03	29.20
	$\bar{\alpha}$	100.65	109.51	108.75	104.21
	κ	0.244	0.275	0.271	0.266
NPP	α_{xx}	150.18	164.64	167.84	165.18
	α_{yy}	174.68	190.81	192.95	187.84
	α_{zz}	148.74	162.23	164.70	162.30
	α_{xy}	29.49	36.94	39.79	39.14
	α_{xz}	-51.94	-61.61	-64.54	-60.80
	α_{yz}	-19.05	-24.89	-27.39	-27.00
	$\bar{\alpha}$	157.87	172.56	175.16	171.77
	κ	0.235	0.260	0.271	0.264
PNP	α_{xx}	145.27	161.30	163.19	151.95
	α_{yy}	166.38	183.18	184.79	166.95
	α_{zz}	140.92	155.23	156.55	144.51
	α_{xy}	-27.08	-34.85	-36.90	-31.58
	α_{xz}	-48.75	-59.34	-61.06	-52.59
	α_{yz}	18.50	24.50	26.31	22.37
	$\bar{\alpha}$	150.86	166.57	168.18	154.47
	κ	0.231	0.258	0.266	0.248
pNA	α_{xx}	89.81	96.27	101.00	100.17
	α_{yy}	97.83	104.71	108.24	102.31
	α_{zz}	98.09	107.11	117.74	123.38
	α_{xy}	2.20	0.92	-3.95	-7.88
	α_{xz}	-34.57	-39.85	-47.37	-51.19

	α_{yz}	25.10	29.41	36.16	38.19
	$\overline{\alpha}$	95.25	102.70	108.99	108.62
	κ	0.261	0.280	0.319	0.349
MNA	α_{xx}	134.98	148.40	165.63	143.93
	α_{yy}	115.71	123.39	125.00	119.19
	α_{zz}	76.57	81.18	84.69	84.80
	α_{xy}	-6.18	-8.08	-14.97	-8.54
	α_{xz}	34.82	40.09	48.48	37.04
	α_{yz}	-5.49	-6.61	-9.85	-6.90
	$\overline{\alpha}$	109.09	117.66	125.11	115.98
	κ	0.246	0.263	0.303	0.243