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On the aromagnetism and anapole moment of anthracene nanocrystals

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Abstract. We report the results of the study of orientation of small anthracene crystals (suspended in liquid) by static and oscillating magnetic fields. They contradict the previous claim that magnetic response of such crystals displays aromagnetism associated with the static toroidal (anapole) moments of the aromatic molecule. The existence of strong aromagnetism in anthracene would be a fundamental result of high importance for the understanding of interactions on the molecular and bio-molecular levels. Instead, our observations are fully consistent with conventional diamagnetism of anthracene molecules.

Although the unusual electromagnetic properties of toroidal (anapole) moments have been discussed in the literature since the mid-fifties [1], we now witness a growing stream of papers on the electrodynamics of toroidal structures. Such structures include close rings of static and oscillating electric or magnetic dipoles and currents flowing on the surface of a torus. More complex arrangements known as super-toroidal structures of different orders, which are in fact fractal complications of the simple toroidal structures have also been investigated [2]. First principles analysis showed that some organic and carbon molecules possess toroidal moments [3]. Recent *ab initio* simulations have revealed the existence of a toroidal moment of polarization in ferroelectric nanodiscs and nanorods [4], while toroidal arrangements of spins have been observed in microscopic ferromagnetic rings and discs [5]. It was also shown that axial toroidal ordering (similar to 'ferromagnetic' or 'weak ferromagnetic') is possible in microscopic crystals with the low-symmetry lattice of triclinic or monoclinic systems [6]. Investigations of localized

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surface plasmons in toroidal nanostructures [7] and interaction of metallic nanotori with a beam of electrons [8] have also been reported. It was shown that interactions between toroidal structures and between toroidal structures and electromagnetic fields could display a number of intriguing properties [9]–[13]. For instance, the strength of such interactions should depend not on the value of the field, but on the value of its time derivatives [6]. It was also claimed that the analysis of the interactions between toroidal currents called for a revision of the reciprocity relations [14]. Oscillating charge–current configurations, which includes toroidal current, were predicted to be non–radiative [2] and recently electromagnetic properties of such non-radiating configurations have been rigorously modelled [15].

Although the importance of toroidal (anapole) moments is already recognized in nuclear and particle physics [16], they are still awaiting direct experimental observation in the frame of classical electrodynamics. So far observation of toroidal moments has been claimed for some multiferroics (such as $Ga_{1.15}Fe_{0.85}O_3$, Cr_2O_3) [17, 18] and also an unconfirmed claim exists for the observation of electronic quantum transitions involving toroidal interaction in solids and in particular unusual behaviour of the optical absorbtion coefficient in the semiconductor-ferroelectric $TlGaSe_2$ near the structural transition point [19]. Detection of toroidal response appears to be a challenging task since toroidal interactions are much weaker than those of dipole type. Nevertheless direct experimental evidence of toroidal response would be extremely important for the development of electrodynamics, in particular because toroidal interaction could play the key role on the molecular and bio-molecular levels.

The first experimental observations of toroidal interactions in classical electrodynamics is believed to be an unexpected magnetic phenomenon exhibited by carbon-based compounds called ‘aromagnetism’, which was reported back in 1990 by Tolstoy and Spartakov [20]. They studied microscopic crystals of several aromatic substances (anthracene, phenanthrene, etc) suspended in water or some other liquid under the influence of an alternating magnetic field. The applied field was either a train of sign-varying square pulses or a rotating field of fixed amplitude. They observed modulation of polarized light passing through a cuvette with the dispersion of microcrystals, which could not be explained simply by diamagnetic reorientation of the aspherical particles. For example, in the case of sign-varying field, the change in transmission began at the time when the field changed sign, and it decayed towards the end of the pulse. The aromagnetism was later suggested to be of a non-magnetic nature [21]. It was attributed to aromatic molecules possessing an axial toroidal moment [1], essentially a ring of static electric dipoles, which could interact with the vortical electric field induced by the alternating magnetic field [6]. The torque acting on an anthracene microcrystal due to this toroidal interaction would be then proportional to the time derivative of the magnetic induction B. The resulting reorientation of the crystals is therefore determined by $\mathrm{d}B/\mathrm{d}t$, which prevails in weak alternating magnetic fields over the diamagnetic term that is proportional to B^2.

In this paper we challenge the experimental results on the reorientation of anthracene crystals in a sign-varying magnetic field as we saw no evidence of aromagnetism. We also show that toroidal interactions are so weak that they cannot be observed in the experiment on magnetic reorientation of aromatic microcrystals. This fact, nevertheless, does not oppose the presence of the toroidal interaction in principle and calls for much more sophisticated experiments for observation of toroidal interactions.

We prepared the dispersion of anthracene crystals using the ‘solvent shifting’ method described in [22]: distilled deionized water (6 ml) was rapidly added to an acetone solution (2 ml) of anthracene ($1.5\,\mathrm{mmol\,l^{-1}}$) while stirring. The concentration of the obtained dispersions

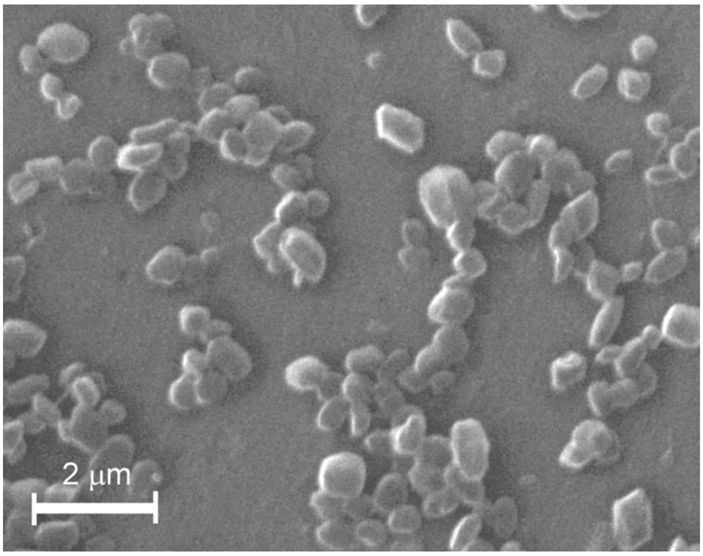

Figure 1. Scanning electron microscope image of anthracene nanocrystals.

was about $3 \times 10^5\,\mathrm{mm}^{-3}$. The shape of the crystals and their size were determined using scanning electron microscopy: the particles were aspherical having the shape of a low aspect ratio parallelogram with an average size of 400 nm (see figure 1). The light scattering properties of such nanocrystals (and consequently the extent to which the light beam will be attenuated) depends on their orientation with respect to the direction of light polarization. This fact is illustrated in figure 2, where we presented images of the nanocrystals made using an optical polarization microscope.

All our experiments with the anthracene nanocrystals were conducted at 20°C and normal atmospheric pressure. We first confirmed diamagnetic reorientation of the nanocrystals by measuring the intensity of linearly polarized light passing through the dispersion in the presence of the static magnetic field in the range from 0 to 0.1 T (toroidal interaction vanishes in a static magnetic field). As a source of light we used a low noise He–Ne laser operating at 633 nm. Measurements were performed in Voigt configuration, in which the direction of light propagation is normal to the magnetic field. The intensity of light increased when the polarization direction and the magnetic field were aligned perpendicularly, and decreased when they were parallel. As expected for a true diamagnetic response, which leads to predominant orientation of the magnetically anisotropic particles in the field, the difference between intensities recorded for two perpendicular polarizations of the incident light was proportional to B^2. In contrast, we did not observe any intensity change when we used an acetone solution of anthracene $0.375\,\mathrm{mmol\,l^{-1}}$, which confirms that the effect is due to reorientation of crystals, but not due to magnetic field induced birefringence or dichroism (Cotton–Mouton effect). We also measured variation of the laser beam intensity while changing the polarization direction of the light with respect to the magnetic field direction. The results of the measurements presented in figure 3 clarify that the nanocrystals tend to orient their longest axis parallel to the magnetic field, which agrees with the fact that the anthracene molecule has its highest diamagnetic susceptibility in the direction perpendicular to the molecular plane. Our observation is also supported by the recent results on reversible orientation of nanocrystals of another aromatic substance perylene [23].

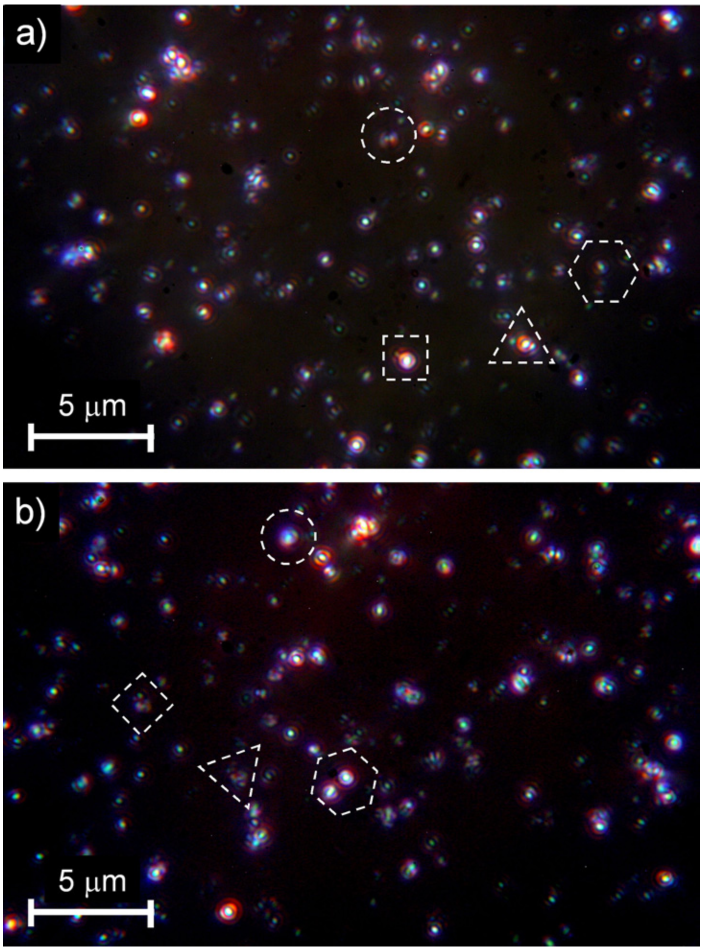

Figure 2. Anthracene nanocrystals under an optical polarization microscope (polarizer and analyser are crossed). Images (a) and (b) are taken at different orientations of the sample with respect to the field of view (orientation of polarizer (analyser) is fixed). Four types of labels (circle, square, triangle and hexagon) are introduced to ease tracing of the crystals which show the most pronounced change in light scattering.

The reorientation of anthracene nanocrystals subjected to a sign-varying magnetic field was studied employing the same optical configuration (Voigt configuration). The polarization of light was set parallel to the magnetic field lines. We used several modulation profiles, namely sinusoidal, square as well as several synthesized meander-like profiles with modulation frequency, f, in the range from 0.3 to 10 Hz. The amplitude of modulation, B_0, varied from about 0.01 to 0.1 T. We did not observe any variation of light intensity when we applied a magnetic field with a square modulation (the rising/falling time of both positive and negative magnetic pulses was about 100 μs). However, a noticeable periodic change in the laser beam intensity at doubled frequency of modulation appeared when the shape of the pulses deviated from square. Figure 4 shows the intensity variation induced by two different types of the distorted square magnetic pulses, at a modulation frequency of 3 Hz.

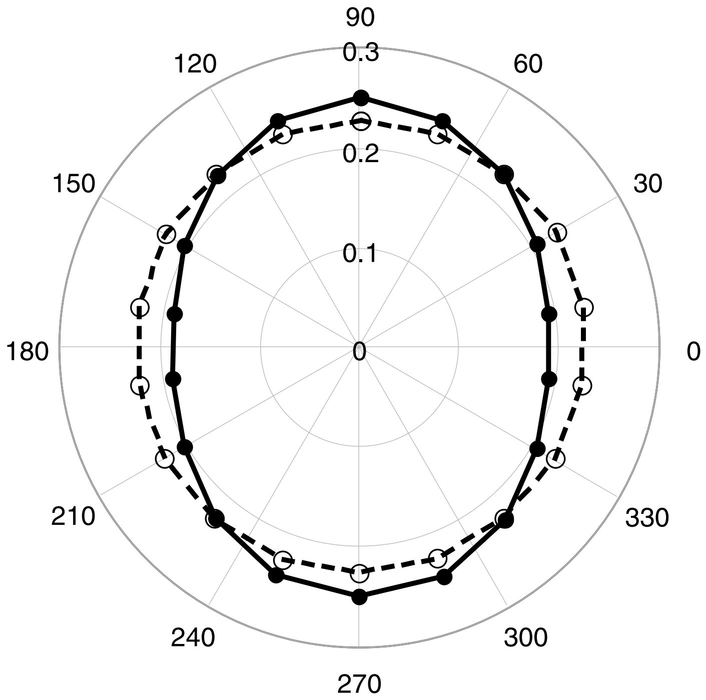

Figure 3. Intensity of the laser beam (in arb. units) transmitted by the dispersion of anthracene nanocrystals as a function of the angle between polarization direction of the light and the magnetic field: dashed line, in the absence of magnetic field; and solid line, under a magnetic field of 0.1 T.

When we applied a sinusoidal magnetic field modulated at 0.3 Hz we detected a clear modulation of the optical signal at 0.6 Hz. The optical modulation also had a sinusoidal profile and was in anti-phase with $B^2(t) = B_0^2 \sin^2(2\pi f t)$. With increasing frequency of the field modulation, a phase delay in optical response with respect to $B^2(t)$ started to build up while the amplitude of the optical modulation decreased. Figure 5 shows the amplitude of the optical modulation as a function of B_0^2 at different modulation frequencies. For all the frequencies and in particular in the region of small amplitudes of the magnetic modulation, i.e. weak magnetic field, where aromagnetism is likely to be the dominant mechanism of the response, we observed no departure from linear dependence.

Clearly the observed behaviour is a result of the diamagnetic anisotropy of the nanocrystals, where variation of B^2 induced a proportional change in the angle of the nanocrystals rotation (i.e. scattering efficiency) thus causing modulation of the laser beam intensity. Correspondingly, when $B^2(t) = \text{const}$ (as in the case of a square modulation profile) no optical modulation was detected. Our experiments with anthracene nano-crystals performed under conditions similar to the results reported in [20] show, contrary to Spartakov and Tolstoy, no evidence of any crystallite reorientation effect proportional to $\mathrm{d}B/\mathrm{d}t$. Therefore our data do not support observation of aromagnetism in this substance.

In fact failure to observe aromagnetism in these experiments is not surprising as the expected strength of the aromagnetic interaction is several orders of magnitude weaker than is necessary

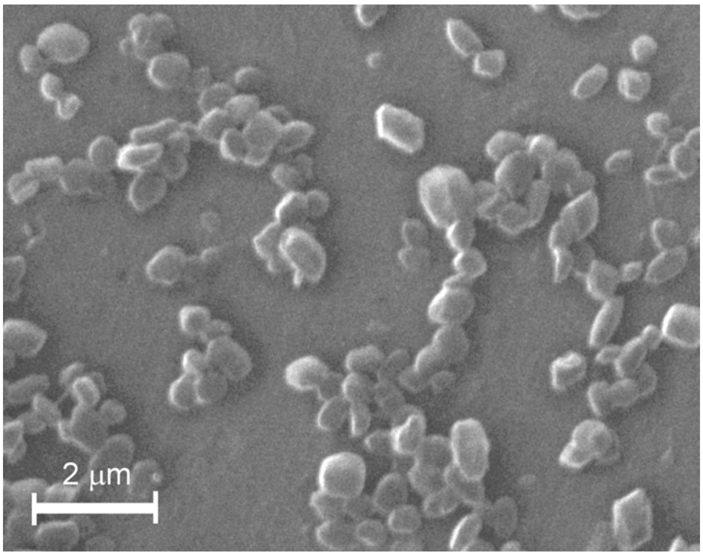

Figure 4. Variation of the laser beam intensity observed for two types of distorted square modulation profiles of the magnetic field at modulation frequency of 3 Hz.

to compete with diamagnetism. Indeed, the torque due to the toroidal interaction is given by [21]

$$\mathbf{L}^{\mathrm{T}} = [\mathbf{g} \times [\nabla \times \mathbf{E}]],$$

where $\mathbf{g}$ is the toroidal moment of the molecule and $\nabla \times \mathbf{E} = -\mathrm{d}\mathbf{B}/\mathrm{d}t$. Toroidal magnetism of the anthracene molecule is justified by the existence of electrical dipole moments forming a closed chain around the molecule. Its value of $g \approx eaR$ was given in [21], where a is the size of a carbon atom (10^{-10} m) and R the radius of a benzene ring (3×10^{-10} m). Since $\mathbf{g}$ is directed normal to the molecular plane the maximum torque in case of a sign-varying magnetic field is achieved when $\mathbf{B}$ is parallel to the molecular plane and its value, $L^{\mathrm{T}}_{\mathrm{max}}$, is given by

$$L^{\mathrm{T}}_{\mathrm{max}} \approx -eaR(\mathrm{d}B/\mathrm{d}t).$$

Having that $\mathrm{d}B/\mathrm{d}t \approx B_0/\Delta t$, where $B_0 < 0.07\,\mathrm{T}$ and $\Delta t < 100\,\mu\mathrm{s}$ we obtained that $|L^{\mathrm{T}}_{\mathrm{max}}| < 3 \times 10^{-36}\,\mathrm{N\,m}$.

The torque acting on the molecule due to the diamagnetic anisotropy can be found using the following formula:

$$\mathbf{L}^{\mathrm{D}} = [\mathbf{m} \times \mathbf{B}].$$

The induced magnetic moment $\mathbf{m} = \chi\mathbf{H}/N_{\mathrm{A}}$, where χ is the tensor of the molar diamagnetic susceptibility of anthracene. Given that the susceptibilities in the plane of the anthracene molecule are almost identical [24] the torque reaches its maximum when magnetic field lines intersect the plane at 45°, thus

$$L^{\mathrm{D}}_{\mathrm{max}} \approx B^2\Delta\chi/2\mu_0 N_{\mathrm{A}},$$

where $\Delta\chi$ is the molar diamagnetic anisotropy of anthracene ($-4\pi \times 173.6 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ [24]). Taking $B_0 = 0.04\,\mathrm{T}$ we get $|L^{\mathrm{D}}_{\mathrm{max}}| \approx 2 \times 10^{-30}\,\mathrm{N\,m}$, which is about six orders of magnitude stronger than characteristic aromagnetic torque.

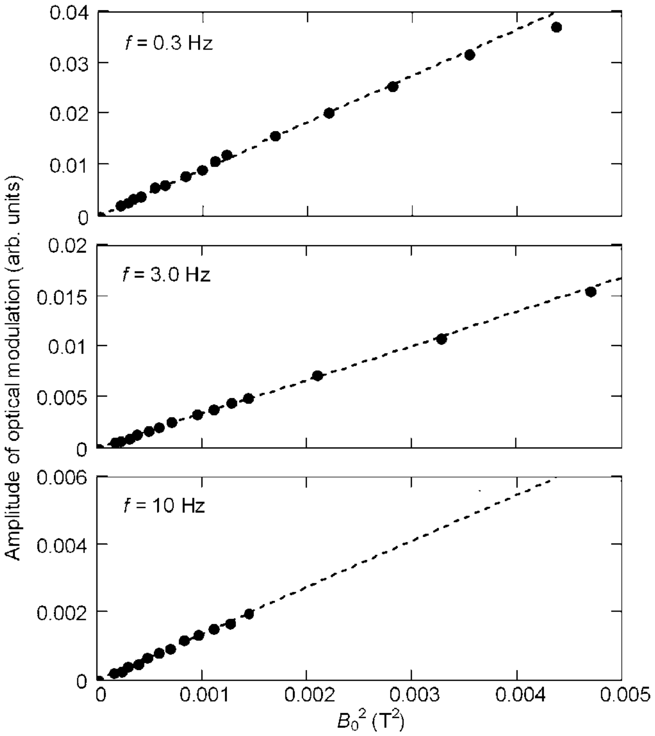

Figure 5. The amplitude of optical modulation as a function of the squared amplitude of magnetic field modulation (sinusoidal profile) at different modulation frequencies.

Toroidal interaction would rotate the anthracene molecule in such a way that the normal to the molecular plane becomes parallel to the magnetic field lines. At the same time, due to diamagnetic anisotropy the molecule tends to orient its normal perpendicular to the field lines. The same would apply for an anthracene crystal where an average direction of the normals to the molecular planes can be introduced. It follows from our estimations that $|L^{\mathrm{D}}_{\max}|$ is at least six orders of magnitude larger than $|L^{\mathrm{T}}_{\max}|$. As there is no reliable evidence of substantial static electric dipoles located at the vertexes of aromatic molecules, the toroidal moment of aromatic molecules is likely to be much smaller than $g \approx eaR$ given in [21] and the toroidal interaction in anthracene is therefore expected to be even weaker than suggested by the estimate.

Thus aromagnetism, if it results from toroidal interaction, should be masked by a much stronger diamagnetic response and could never be observed neither in [20] nor in our experiment unless it has a different nature. Our measurements, however, suggest that at the prescribed experimental conditions there can be no strong effects other then diamagnetism. This also applies to other aromatic substances such as phenanthrene, pyrene, triphenylene, naphthalene, perylene, etc as they have diamagnetic properties similar to those of anthracene and toroidal moments of the aromatic molecules are expected to be of the same order.

It should be noted that the magnitude of toroidal response of the anthracene nanocrystals can in principle be made as strong as the magnitude of the diamagnetic effect observed in our experiment. To achieve this one needs to exploit the difference in dependencies of the competing phenomena on the magnetic field. Indeed, the diamagnetic response depends on the field as B^2 while the toroidal response is proportional to $\mathrm{d}B/\mathrm{d}t$. Therefore, if the frequency of modulation of the magnetic field is increased to 1 GHz without reducing its magnitude, the toroidal response could be as strong as the diamagnetic response, which would make it detectable in the light scattering experiment. In practice, however, producing a rapidly oscillating magnetic field is extremely difficult due to inductance of the magnetic coils and therefore detection of the toroidal response through magnetic field-induced reorientation of nanocrystals and light-scattering shall be very hard. A more realistic proposition to study toroidal response would be perhaps to employ a metamaterials approach. It emerged very recently that resonant interaction of electromagnetic radiation with arrays of artificially manufactured toroidal wire structures can result in an observable toroidal response detected through resonant transmission losses of electromagnetic radiation [25].

In conclusion, we failed to confirm the existence of an aromagnetic response, which was previously reported to have been observed in a range of aromatic substances in the form of small crystals dispersed in a liquid. Our estimations show that if it resulted from so-called toroidal interaction it could not be observed experimentally. This fact, however, does not oppose the existence of the toroidal interaction in aromatic substances, which can simply be masked by the much stronger diamagnetism.

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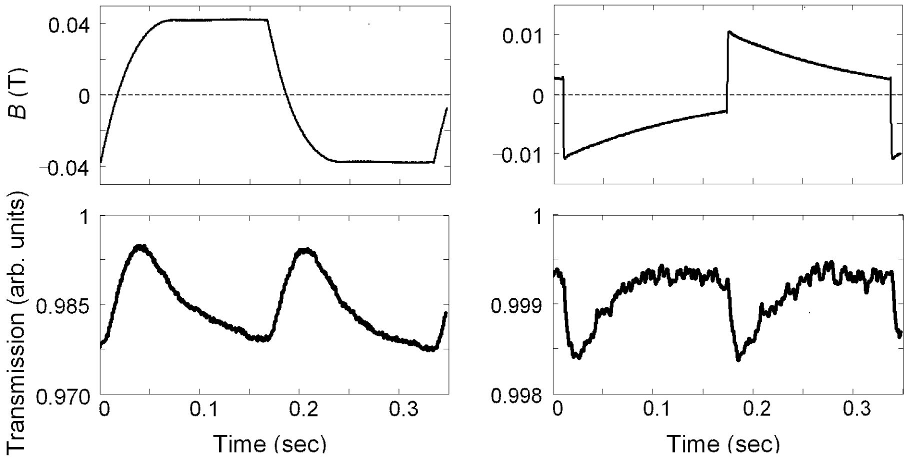
Erratum added 2 July 2007

Due to a typesetting error, figure 4 in this article is actually a repeat of figure 1. The correct figure 4 is given below.



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